# Thermodynamics & Statistical Physics

*for*

## CSIR-UGC-NET & GATE

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# Chapter 1

# Basic Introduction

## Basics of Thermodynamics

This is the branch of Physics in which we deal with **internal macroscopic state of the system.**

**System :** Any portion of matter which is considered as **separated from its surrounding** is called system.

**Surrounding :** All these things which are outside the system and influence its behaviour are known as surrounding.
**Example :** Let a gas be filled in a cylinder fitted with a piston heated by a burner. Here the gas is the system while the piston and burner are the surroundings.

**Thermodynamic system :** A thermodynamic system is one which may interact with its surrounding in atleast two distinct ways and one of these necessarily a transfer of heat(In or out of the system) and the other may be some other means of transfer of energy say be performance of mechanical work by or on the system through electromagnetic interaction.

**Example:** Gas contained in a cylinder, vapour in contact with its liquid stretched wire.
**Equilibrium :** If there is no change in the property of the system w.r.t. time, the system is called in equilibrium.

1. **Mechanical equilibrium :** When there is no unbalanced force interior of the system and between the system and surrounding then the system is in mechanical equilibrium.
   **Example:** Ideal gas inside a container.

2. **Chemical equilibrium :** If the system has no tendency to undergo a change in internal structure and also has no tendency to transfer matter from one part to another part then it is said to be in chemical equilibrium.

3. **Thermal equilibrium:** If there is no temperature difference between any part of the system and also not between the system & surrounding then the system is in thermal equilibrium.

4. **Thermodynamic equilibrium:** A system is said to be in thermodynamical equilibrium if its state doesn't change in any way i.e. mechanical, chemical & thermal equilibrium.

If however the conditions for any one of three type of equilibrium are not satisfied then the system is said to be in non thermodynamic equilibrium. If all are not satisfied then system is called in non-equilibrium.

**Microscopic parameter :** The parameter of the order of atomic level is called microscopic parameter. There are parameters that describes the internal structure of the system or associated with the constituent of the system. These parameters can't be directly measured in laboratory and can't be experience by our sense of perception.
**Example:** mass, velocity, energy, momenta, magnetic moment of constituent (atom or molecule) of the system.
**Macroscopic parameter:** Macroscopic parameter of a system are the average of the sum total of the corresponding microscopic parameter of the constituent particles. These can be measured directly in the laboratory and can be directly experienced by our sense of perception.
**Example:** pressure, volume, temperature, entropy

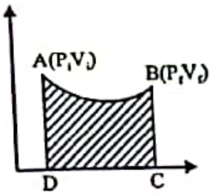
**Microstate:** The state of the system associated with the states of all constituents of the system is called microstate or microscopic state.

**Macroscopic State :** The state of the system associated with the parameters of the whole system is called macrostate. The macrostate is called thermodynamic state.

A thermodynamic system is taken from initial to final state the work done by the system is given by

$$dW = FdS = PAdS = PdV$$

$$W = \int_{\text{initial}}^{\text{final}} dW = \int_i^f PdV$$



work done on the system is – ve

work done by the system is + ve

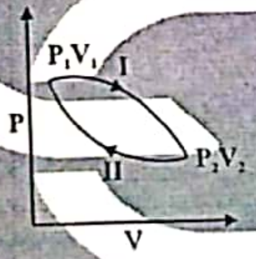
work done = Area under the curve (on PV diagram)

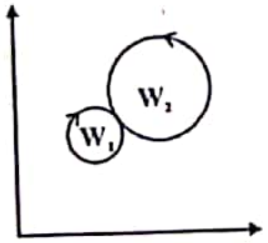
work done depends on the path and can't be written as perfect differential. Similarly, heat also depends on path and can't be written as perfect differential.

P, V, T, U, S are exact or perfect differential (state or point function)

**Cyclic Process :** When a system undergoes a change from initial state to another final state through different states and come back to initial state then the process is called cyclic process.

Work done in cyclic process is equal to area enclosed by the cycle. If the cycle is traced anticlockwise work done is –ve i.e. work done on the system. If the cycle is traced clockwise then workdone is +ve i.e work done by the system.



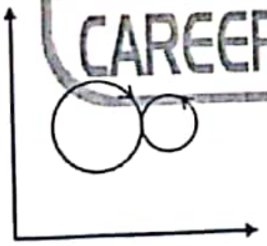


$W_1 < W_2$ $W = W_2 - W_1$

$W_2$ is anticlockwise

$W_1$ is clockwise

So work done on the system

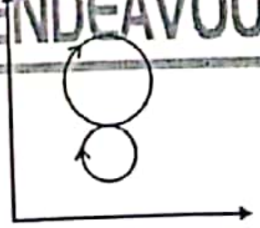


$W = W_1 + W_2$

$W_1$ is clockwise and

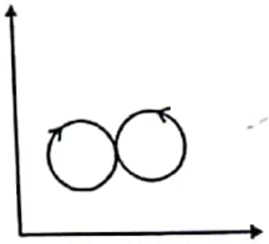
$W_2$ is anticlockwise

So, work done by the system



$W = W_1 + W_2$

$W_1$ is clockwise and $W_2$ also work done by the system



$W_1 = W_2$

work done is zero

**Internal energy :** The internal energy is the energy associated with microscopic mechanical energy

$$I.E. = K.E. + P.E.$$

It is impossible to divide internal energy into a thermal and mechanical part

Let Q be the heat absorbed by the system and W be the work done by the system during the process that leads the system from initial state to final state Q – W is calculated then Q – W is same for different path although Q & W individually are different for different path. Then this is called change in internal energy dU.

$$dU = Q - W$$

Q – W depend only on state (initial and final) and not on the path. The internal energy of a system in a given state is a function of that state only and doesn't at all depend upon the way by which that states has been acquired.

Hence we can't tell whether the internal energy of the system has been acquired by heat transfered or by performance of mechanical work or by both.

**The Kinetic Theory of Gases**

We can summarize the kinetic theory of gases with four basic postulates:

1. **Gases are made up of molecules:** We can treat molecules as point masses that are perfect spheres. Molecules in a gas are very far apart, so that the space between each individual molecule is many orders of magnitude greater than the diameter of the molecule.
2. **Molecules are in constant random motion:** There is no general pattern governing either the magnitude or direction of the velocity of the molecules in a gas. At any given time, molecules are moving in many different directions at many different speeds.
3. **The movement of molecules is governed by Newton's Laws:** In accordance with Newton's First Law, each molecule moves in a straight line at a steady velocity, not interacting with any of the other molecules except in a collision. In a collision, molecules exert equal and opposite forces on one another.
4. **Molecular collisions are perfectly elastic:** Molecules do not lose any kinetic energy when they collide with one another.

The kinetic theory projects a picture of gases as tiny balls that bounce off one another whenever they come into contact. This is, of course, only an approximation, but it turns out to be a remarkably accurate approximation for how gases behave in the real world. These assumptions allow us to build definitions of temperature and pressure that are based on the mass movement of molecules.

- **Gas Laws**
  Boyles Law : PV = constant
  Charles Law : V/T = constant
- **Ideal Gas Equation**
  PV = nRT
- **Dalton Law of Partial Pressure**
  $P = P_1 + P_2 + P_3$
  Pressure exerted by n moles of an ideal gas in terms of the speed of the molecules

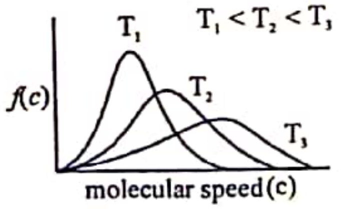
$$P = \frac{nM\,(v_{rms})^2}{3V}$$

- **Maxwell Speed Distribution Function:**
  The number of particle moving with velocity c and $c + dc$ is given by

$$dN_c = 4\pi N\left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-\frac{mc^2}{2k_BT}}c^2dc$$

where N is the total number of gas particles and

$$f(c) = 4\pi\left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-\frac{mc^2}{2kT}}c^2$$ is called Maxwell's distribution function.



Average speed, r.m.s speed and most probable speed:

**Average speed :** $\bar{c} = \frac{1}{N}\int_0^\infty c\,dN_c = \sqrt{\frac{8k_BT}{\pi m}}$

**R.M.S speed :** $c_{rms} = \sqrt{\frac{1}{N}\int_0^\infty c\,dN_c} = \sqrt{\frac{3k_BT}{m}}$

**Most probable speed:**

$$\left.\frac{df}{dc}\right|_{c=c_m} = 0$$

We get, $c_m = \sqrt{\frac{2k_BT}{m}}$

$$\bar{c} : c_{rms} : c_m = \sqrt{\frac{8k_BT}{\pi m}} : \sqrt{\frac{3k_BT}{m}} : \sqrt{\frac{2k_BT}{m}}$$

$$\Rightarrow \quad \boxed{c_m : \bar{c} : c_{rms} = 1 : 1.128 : 1.224}$$

**Q.** Five gas molecules chosen at random are found to have speeds of 500, 600, 700, 800 and 900 m/s? What is the rms speed and average speed?

(a) $v_{rms}$=700 m/s and $v_{av}$=714 m/s (b) $v_{rms}$=71.4 m/s and $v_{av}$=70.4 m/s

(c) $v_{rms}$=714 m/s and $v_{av}$=700 m/s (d) $v_{rms}$=70.4 m/s and $v_{av}$=71.4 m/s

**Soln.** Given : $v_1 = 500$ m/s, $v_2 = 600$ m/s, $v_3 = 700$ m/s, $v_4 = 800$ m/s, $v_5 = 900$ m/s

$$v_{avg.} = \frac{\sum_{i=1}^{5} v_i}{5} = \frac{500+600+700+800+900}{5} = 700 \text{ m/s}$$

$$\text{and } v_{r.m.s.} = \left(\frac{\sum_{i=1}^{5} v_i^2}{5}\right)^{1/2} = \left(\frac{500^2+600^2+700^2+800^2+900^2}{5}\right)^{1/2} = 714.14 \text{ m/s}$$

**Correct option is (c)**

**Maxwell's distribution function in momentum and energy form:**

The number of particles moving with energy $E$ and $E+dE$ is given by

$$dN_E = 2N\left(\frac{E}{\pi}\right)^{1/2} (k_BT)^{-3/2}\, e^{-E/k_BT}\, dE$$

The number of particle moving momentum $p$ and $dp$ is given by

$$dN_P = 4\pi N\left(\frac{1}{2\pi m k_BT}\right)^{3/2} e^{-\frac{p^2}{2mk_BT}}\, p^2\, dp$$

## Degree of Freedom

**(a) Definition :** It is defined as the total number of independent variables required to describe completely the state of motion of a body. It can be calculated as

$$f = 3N - C,$$

where $N$ represents the number of particles [atoms in case of molecules] and $C$ represents the number of constraints [bonds or lone pairs in case of molecules].

Different molecules have various types of degree of freedom corresponds to various types of motion they perform like translation, rotation and vibration. When the molecules are at low temperature, they exhibit only translational motion and hence have only translational degree of freedom. When the temperature increases, they also perform rotational motion along with the translational motion and hence possesses degree of freedom corresponds to both type of motion. When the temperature is sufficiently high, the bonds get weaker and causes the molecules to vibrate along with both translational and rotational motion.

The degree of freedom for various molecules can be calculated as :

**(a) For monoatomic molecules** [e.g., Ar, Xe, Rn, He].

Each molecule contains one atom and has no bond. So, $N = 1$ and $C = 0$.

Therefore, $f = 3 \times 1 - 0 = 3$.

All these three degree of freedom corresponds to translational degree of freedom.

**(b) For diatomic molecules** [e.g., $O_2$, $N_2$, $H_2$].

Since each diatomic molecule contains two atoms, we have $N = 2$.

**(i) At low temperature :** The bond between the two atoms remain rigid and hence there is only one constraints.

Therefore, $f = 3 \times 2 - 1 = 5$.

Out of these 5, 3 corresponds to translational motion and 2 corresponds to vibration motion.

**(ii) At high temperature :** The bond between the atoms do not remain rigid causing the atoms to vibrate as well and hence there is no constraints at high temperature.

Therefore, $f = 3 \times 2 - 0 = 6$.

In this 3 corresponds to translational, 2 corresponds to rotation and the remaining 1 corresponds to vibrational motion.

**(c) For linear triatomic molecules** [e.g., $CO_2$, $N_2O$].

Since each linear triatomic molecule has three atoms, we have $N = 3$.

**(i) At low temperature :** Since there are two bonds, the number of constraints will be two.

Therefore, $f = 3 \times 3 - 2 = 7$.

Out of these 7, 3 corresponds to translation, 2 corresponds to rotation [as the molecules are linear] and the remaining 2 are because of vibrational motion. But if the molecules have rigid bonds, these two vibrational degree of freedom are not active.

**(ii) At high temperature :** The bonds will not remain constraints and hence $C = 0$.

Therefore, $f = 3 \times 3 - 0 = 9$.

Out of these 9, 3 corresponds to translation, 2 corresponds to rotation and the remaining 4 corresponds to vibrational mode.

**(d) Non-linear triatomic molecules** [e.g., $O_3$, $H_2O$].

Since each non-linear triatomic molecules has three atoms, we have $N = 3$.

**(i) At low temperature :** The three bonds will behave as three constraints. So, we have

$f = 3 \times 3 - 3 = 6$.

The three, here, corresponds to translational and the remaining three corresponds to rotation [as the molecule is non-linear].

**(ii) At high temperature :** The bonds will not remain constraints. So, we have

$f = 3 \times 3 - 0 = 9$.

The three will corresponds to translation, three to rotational and the remaining three will corresponds to vibration.

In general, the degree of freedom can be distributed as :

(i) **At low temperature :**

| Types of molecule → Mode ↓ | Linear molecule | Non-linear molecule |
|---|---|---|
| Translation | 3 | 3 |
| Rotation | 2 | 3 |
| Vibration | $3N-C-5$ | $3N-C-6$ |

**(ii) At high temperature :**

| Types of molecule → Mode ↓ | Linear molecule | Non-linear molecule |
|---|---|---|
| Translation | 3 | 3 |
| Rotation | 2 | 3 |
| Vibration | $3N-5$ | $3N-6$ |

## Law of Equipartition of Energy

For 1-D, the Maxwell's velocity distribution function is $f(v)=\left(\frac{m}{2\pi k_BT}\right)^{1/2} e^{-\frac{mv^2}{2k_BT}}$, $-\infty<v<\infty$

So, average kinetic energy is

$$\bar{E}=\frac{\int_{-\infty}^{\infty} Ef(v)\,dv}{\int_{-\infty}^{\infty} f(v)\,dv}=\frac{\int_{-\infty}^{\infty}\frac{1}{2}mv^2\left(\frac{m}{2\pi k_BT}\right)^{1/2} e^{-\frac{mv^2}{2k_BT}}dv}{\int_{-\infty}^{\infty}\left(\frac{m}{2\pi k_BT}\right)^{1/2} e^{-\frac{mv^2}{2k_BT}}dv}$$

$$=\frac{m}{2}\frac{\int_{-\infty}^{\infty} v^2 e^{-\frac{mv^2}{2k_BT}}dv}{\int_{-\infty}^{\infty} e^{-\frac{mv^2}{2k_BT}}dv}=\frac{m}{2}\frac{\int_{0}^{\infty} v^2 e^{-\frac{mv^2}{2k_BT}}dv}{\int_{0}^{\infty} e^{-\frac{mv^2}{2k_BT}}dv}$$

Using $\int_0^{\infty} x^n e^{-ax^2}dx=\frac{\Gamma\left(\frac{n+1}{2}\right)}{2a^{\frac{n+1}{2}}}$, we have

$$\Rightarrow\ \bar{E}=\frac{m}{2}\frac{\Gamma\left(\frac{3}{2}\right)\Big/2\left(\frac{m}{2k_BT}\right)^{3/2}}{\Gamma\left(\frac{1}{2}\right)\Big/2\left(\frac{m}{2k_BT}\right)^{1/2}}=\frac{m}{2}\frac{\frac{1}{2}\sqrt{\pi}}{\sqrt{\pi}}\frac{2k_BT}{m}\ \Rightarrow\ \bar{E}=\frac{1}{2}k_BT$$

**(a) Statement :** In thermal equilibrium, any degree of freedom (such as component of the position or velocity of a particle) which appears only "quadratically" in the energy has an average energy per molecule of

$$\frac{1}{2}k_BT.$$

This is the *law of equipartition of energy*.

**(b) Examples :**

**(i) A free particle of mass $m$ moving in $xy$-plane**

The Hamiltonian will be

$$H=\frac{p_x^2}{2m}+\frac{p_y^2}{2m}$$

Since there are two quadratic terms, the average thermal energy is

$$\langle E\rangle = 2\times\frac{1}{2}k_BT = k_BT$$

**(ii) A free particle rotating in $xy$-plane about $z$-axis**

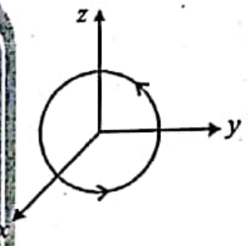
The corresponding Hamiltonian is

$$H=\frac{L_z^2}{2I},$$

where $I$ is the moment of inertia of the particle about $z$-axis.

Therefore, the average thermal energy is

$$\langle E\rangle = 1\times\frac{1}{2}k_BT = \frac{1}{2}k_BT$$



**(iii) A one-dimensional harmonic oscillator in $x$-axis**

The corresponding Hamiltonian is

$$H=\frac{p_x^2}{2m}+\frac{1}{2}kx^2,$$

where $k$ is the spring's constant.

Therefore, the average thermal energy is

$$\langle E\rangle = 2\times\frac{1}{2}k_BT = k_BT$$

**(c) Other statement :** The law of equipartition of energy, therefore, can be re-stated as :

"The average energy corresponds to each translational degree of freedom is $\frac{1}{2}k_BT$, corresponds to each rotational degree of freedom is $\frac{1}{2}k_BT$ and corresponds to each vibrational degree of freedom is $k_BT$".

Mathematically, $\boxed{\langle E\rangle = f_{\text{Translation}}\times\frac{1}{2}k_BT + f_{\text{Rotation}}\times\frac{1}{2}k_BT + f_{\text{Vibration}}\times k_BT}$.

**Q.** Calculate the average thermal energy of a diatomic molecule in both low temperature and high temperature condition.

**Soln.** (i) At low temperature, we have

$f_{\text{Translational}}=3$ and $f_{\text{Rotation}}=2$.

Therefore, $\langle E\rangle = 3\times\frac{1}{2}k_BT + 2\times\frac{1}{2}k_BT = \frac{5}{2}k_BT$.

(ii) At high temperature, we have

$$f_{\text{Translational}} = 3,\ f_{\text{Rotation}} = 2 \text{ and } f_{\text{Vibration}} = 1.$$

Therefore, $\langle E\rangle = 3\times\frac{1}{2}k_BT + 2\times\frac{1}{2}k_BT + 1\times k_BT = \frac{7}{2}k_BT$

*Note* : The formula for average thermal energy per particle as $\langle E\rangle = \frac{f}{2}k_BT$ is valid only when there is no vibrational mode.

**Q.** A vessel contains a mixture of one mole of oxygen and two moles of nitrogen at 300 K. The ratio of the average rotational kinetic energy per $O_2$ molecule to per $N_2$ molecule is

(a) 1 : 1 (b) 1 : 2 (c) 2 : 1

(d) depends on the moment of inertia of the two molecules

**Soln.** Since both the gases are diatomic, both will have the same number of rotational degree of freedom i.e., two. Therefore, both the gases will have the same average rotational kinetic energy per molecule = 2 × 1/2 $k_BT$ or $k_BT$. Thus ratio will be 1 : 1.

**Correct option is (a)**

**Q.** A gas mixture consists of 2 moles of oxygen and 4 moles of argon at temperature T. Neglecting all vibrational modes, the total internal energy of the system is

(a) 4 RT (b) 15 RT (c) 9 RT (d) 11 RT

**Soln.** Internal energy of $n$ moles of an ideal gas with no vibrational degree of freedom at temperature $T$ is given by

$$U = n\left(\frac{f}{2}RT\right)$$

where, $f$ = degree of freedom.

= 5 for $O_2$ and 3 for Ar

Hence, $U = U_{O_2} + U_{Ar} = 2\left(\frac{5}{2}RT\right) + 4\left(\frac{3}{2}RT\right) = 11\,RT.$

**Correct option is (d)**

**Q.** In 1-dimension, an ensemble of $N$ classical particles has energy of the form $E = \frac{p_x^2}{2m} + \frac{1}{2}kx^2$. The average internal energy of the system at temperature $T$ is

(a) $\frac{3}{2}Nk_BT$ (b) $\frac{1}{2}Nk_BT$ (c) $3Nk_BT$ (d) $Nk_BT$

**Soln.** The given Hamiltonian is

$$E = \frac{p_x^2}{2m} + \frac{1}{2}kx^2$$

According to equipartition theorem, the contribution of each quadratic term in Hamiltonian to average thermal energy is $\frac{1}{2}k_BT$. So the average thermal energy of one particle is .

$$U_1 = \frac{1}{2}k_BT + \frac{1}{2}k_BT = k_BT$$

$\therefore$ Average thermal energy of $N$-particle system is $U = NU_1 = Nk_BT$

**Correct answer is (d)**

**Q.** A classical gas of molecules each of mass m, is in thermal equilibrium at the absolute temperature, T. The velocity components of the molecules along the Cartesian axes are $v_x$, $v_y$ and $v_z$. The mean value of $(v_x + v_y)^2$ is:

(a) $\frac{k_BT}{m}$ (b) $\frac{3}{2}\frac{k_BT}{m}$ (c) $\frac{1}{2}\frac{k_BT}{m}$ (d) $\frac{2k_BT}{m}$

**Soln.** $\langle (v_x + v_y)^2\rangle = \langle v_x^2\rangle + \langle v_y^2\rangle + 2\langle v_x v_y\rangle$

Putting $\langle v_x^2\rangle = \langle v_y^2\rangle = \langle v_z^2\rangle = \frac{k_BT}{m}$ $\left[\because \frac{1}{2}mv^2 = \frac{1}{2}m(v_x^2 + v_y^2 + v_z^2) = \frac{3}{2}k_BT\right]$

and $\langle v_x v_y\rangle = 0$

So, $\langle (v_x + v_y)^2\rangle = \frac{k_BT}{m} + \frac{k_BT}{m} + 0 = \frac{2k_BT}{m}$

**Correct option is (d)**

- **Vander Waals equation**

$$\left(\frac{P+a}{V^2}\right)(V-a) = nRT$$

**Mean free path** is given by $\lambda = k_BT/\sqrt{2}\pi\sigma^2 P$ (where $\sigma$ is the diameter of the molecule).

## PREVIOUS YEARS SOLUTIONS OF TIFR

**Q.** Consider the CO molecule as a system of two point particles which has both translational and rotational degrees of freedom. Using classical statistical mechanics, the molar specific heat $C_V$ of CO gas is given in terms of the Boltzmann constant $k_B$ by **[TIFR 2014]**

(a) $\frac{5}{2}k_B$ (b) $2k_B$ (c) $\frac{3}{2}k_B$ (d) $\frac{1}{2}k_B$

**Soln.** For diatomic molecule, we have

$f_{\text{translation}} = 3$ and $f_{\text{rotational}} = 2$.

The average energy is

$$\langle U\rangle = \left(\frac{f_{\text{translational}}}{2} + \frac{f_{\text{rotational}}}{2} + f_{\text{Vibrational}}\right) \times k_BT = \frac{5}{2}k_BT.$$

Therefore, $C_v = \frac{d}{dt}\langle U\rangle = \frac{5}{2}k_B$.

**Correct option is (a)**

**Q.** Two containers are maintained at the same temperature and are filled with ideal gases whose molecules have mass $m_1$ and $m_2$ respectively. The mean speed of molecules of the second gas is 10 times the r.m.s. speed of the molecules of the first gas. Find the ratio of $m_1/m_2$, to the nearest integer. **[TIFR 2016]**

**Soln.** Given : $(v_{\text{mean}})_2 = 10\,(v_{\text{r.m.s}})_1$

$$\Rightarrow \sqrt{\frac{8}{\pi}\frac{k_BT}{m_2}} = 10\sqrt{\frac{3k_BT}{m_1}}$$

$$\Rightarrow \frac{m_1}{m_2} = \frac{100 \times 3\pi}{8} = 117.8 \approx 118 \text{ (nearest integer).}$$

**Correct answer is (118)**

## PREVIOUS YEARS SOLUTIONS OF JEST

**Q.** Electrons of mass $m$ in a thin, long wire at a temperature $T$ follow a one-dimensional Maxwellian velocity distribution. The most probable speed of these electrons is, **[JEST 2015]**

(a) $\sqrt{\left(\frac{kT}{2\pi m}\right)}$ (b) $\sqrt{\left(\frac{2kT}{m}\right)}$ (c) 0 (d) $\sqrt{\left(\frac{8kT}{\pi m}\right)}$

**Soln.** The one-dimensional Maxwellian distribution for speed is

$$f(v)=2\left(\frac{m}{2\pi k_B T}\right)^{1/2} e^{-\frac{mv^2}{2k_BT}}\ ;\ 0<v<\infty$$

For most probable speed $(v=v_p)$, we have

$$\left.\frac{d}{dv}f(v)\right|_{v=v_p}=0\Rightarrow v_p=0.$$

**Correct option is (c)**

**Q.** For which gas the ratio of specific heats $(C_p/C_v)$ will be largest? **[JEST 2014]**

(a) mono-atomic (b) di-atomic (c) tri-atomic (d) hexa-atomic

**Soln.** The ratio of specific heat is

$$\frac{C_p}{C_v}=\frac{\left(\frac{f}{2}+1\right)R}{\frac{f}{2}R}\text{, where } f \text{ is the degree of freedom for the gas}$$

$$=1+\frac{2}{f}.$$

Since $f$ is minimum for mono-atomic gas, i.e., $f=3$, $C_p/C_v$ will be largest for mono-atomic gas.

**Correct option is (a)**

# Chapter 2

# Laws of thermodynamics & their Consequences-1

## Laws of Thermodynamics

**Zeroth law of thermodynamics :**

If two systems are separately in thermal equilibrium with a third system they are also in thermal equilibrium with each other.

This law enables us to compare the temperature of two system with the help of third system. This law can be used to define temperature.

The temperature of a system is the property which determines whether or not a system is in thermal equilibrium with other system.

**First law of thermodynamics :**

The first law of thermodynamics is simply the principle of conservation of energy applied to the system. Whenever other forms of energy is converted into heat and viceversa there is a fixed ratio between quantities of energy & heat thus converted.

If an infinitesimal amount of heat dQ is given to the system then its some part is used to do work (dW) and other part is used to change the internal energy (dU)

$$dQ = dU + dW$$

**Significance :** This law signifies that

(i) Heat is a form of energy

(ii) Energy is conserved in thermodynamic system.

(iii) Every thermodynamic system in equilibrium state possess internal energy which is a function of state only. This law signifies the exact relation between heat & other energy. It follows directly from this law that it is impossible to derive any work without expenditure of an equal amount of energy in some other form.

**First law of Thermodynamics in different process :**

**(i) Cyclic Process :**

$$dQ = dU + dW$$

For cyclic process $dU = 0$, because internal energy depends only on the state.

$$\int dQ = \int dW$$

**ii) Isochoric Process : ( $dV = 0$ )**

$$dQ = dU + dW \quad \text{but} \quad dW = 0\text{, because } V = \text{constant} \quad dQ = dU$$

If heat is given to the system internal energy increase & if heat is given by the system, internal energy decrease.

**iii) Adiabatic Process : ( $dQ = 0$ )**

$$dQ = dU + dW \quad \text{or} \quad Q = \text{constant} \Rightarrow dQ = 0$$

$$dU + dW = 0 \quad \text{or} \quad dU = -dW = -PdV$$

If work is done by the system (in adiabatic process) then internal energy decreases & vice-versa.

**iv) Free expansion :**

If a system, say, a gas expands in such a way that no heat enters or leave the system (adiabatic process) and also no work is done by or on the system then the process is called free expansion.

For free expansion $dQ = 0$ and $dW = 0$

$$\Rightarrow dU = 0 \qquad \text{or} \qquad U = \text{constant}$$

The initial and final state internal energy are same.

**Q.** **A perfectly insulated box contains a partition dividing the box into two equal parts as shown in the figure.**

**Initially L.H.S. part contain an ideal monoatomic gas at temperature T and other half is evacuated. The partition is suddenly removed so that the gas is filled through out the entire box.**

**(a) What is the final temperature of the gas**

**(b) What is the change in internal energy.**

**(c) What is the work done.**

**Soln.** $dQ = dU + dW$

Since there is no transfer of heat $dQ = 0$

$P = 0,\ dW = 0,\ \Rightarrow dU = 0$

If internal energy is same, change in temperature is zero $T_1 = T_2$.

**Q.** **Show that** $\left(\frac{\partial \alpha}{\partial P}\right)_T + \left(\frac{\partial \beta}{\partial T}\right)_P = 0$

**Where α and β are the coefficient of thermal expansion and coefficient of compressibility respectively.**

**Soln.** Since V is a state function so we can write

$$\left[\frac{\partial}{\partial T}\left(\frac{\partial V}{\partial P}\right)_T\right]_P = \left[\frac{\partial}{\partial P}\left(\frac{\partial V}{\partial T}\right)_R\right]_T$$

or $$\left[\frac{\partial}{\partial T}(-V\beta)\right]_P = \left[\frac{\partial}{\partial P}(V\alpha)\right]_T \qquad \boxed{-\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T = \beta \quad \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = \alpha}$$

carrying out the differentiation we get

$$-\beta\left(\frac{\partial V}{\partial T}\right)_P - V\left(\frac{\partial \beta}{\partial T}\right)_P = \alpha\left(\frac{\partial V}{\partial P}\right)_T + V\left(\frac{\partial \alpha}{\partial P}\right)_T$$

or $$-\frac{\beta}{V}\left(\frac{\partial V}{\partial T}\right)_P - \left(\frac{\partial \beta}{\partial T}\right)_P = \frac{\alpha}{V}\left(\frac{\partial V}{\partial P}\right)_T + \left(\frac{\partial \alpha}{\partial P}\right)_T$$

$$\left(\frac{\partial \alpha}{\partial P}\right)_T + \left(\frac{\partial \beta}{\partial T}\right)_P = -\frac{\beta}{V}\left(\frac{\partial V}{\partial T}\right)_P - \frac{\alpha}{V}\left(\frac{\partial V}{\partial P}\right)_T = -\frac{\beta}{V}(\alpha V) - \frac{\alpha}{V}(-\beta V) = 0$$

**Q.** **Show that for homogeneous fluid** $C_P - C_V = T\left(\frac{\partial P}{\partial T}\right)_V\left(\frac{\partial V}{\partial T}\right)_P$ **where the symbols have their usual meaning.**

**(a) Hence prove that for a perfect gas**

$$C_P - C_V = R$$

**(b) Hence prove for a vander Waals' gas**

$$C_P - C_V = R\,(1 + 2a/RTV)$$

**Soln.** The specific heat at constant pressure and constant volume are given as

$$C_P = \left(\frac{\partial Q}{\partial T}\right)_P = T\left(\frac{\partial S}{\partial T}\right)_P \qquad [dQ = TdS]$$

$$C_V = \left(\frac{\partial Q}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V$$

Now if the entropy S is regarded as a function of T and V and since dS is perfect differential
$S = S(T, V)$

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$

$$\left(\frac{\partial S}{\partial T}\right)_P = \left(\frac{\partial S}{\partial T}\right)_V + \left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P$$

$$T\left(\frac{\partial S}{\partial T}\right)_P = T\left(\frac{\partial S}{\partial T}\right)_V + T\left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P$$

From Maxwell's I$^{st}$ relation $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$

$$\therefore \quad T\left(\frac{\partial S}{\partial T}\right)_P = T\left(\frac{\partial S}{\partial T}\right)_V + T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P$$

Now $$C_P - C_V = T\left(\frac{\partial S}{\partial T}\right)_P - T\left(\frac{\partial S}{\partial T}\right)_V = T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P \qquad \ldots(1)$$

**(a)** For a perfect gas the equation of state is PV = RT (one mole)

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V} \qquad \left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P}$$

$$C_P - C_V = T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P = T\left(\frac{R}{V}\right)\left(\frac{R}{P}\right) = \frac{TR^2}{PV} = \frac{R^2T}{RT} = R$$

**(b)** For a vander Waals' gas the equation of state is

$$\left(P + {}^{a}\!/_{V^2}\right)(V - b) = RT \quad \text{(one mode)}$$

or $$\left(P + \frac{a}{V^2}\right) = \frac{RT}{V - b} \qquad \ldots(2)$$

where a and b are constant
Differentiating eq$^n$ (2) w.r.t. T at constant volume we get

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V - b}$$

Differentiating eq$^n$ (2) w.r.t. T at constant pressure we get

$$0 - \frac{2a}{V^3}\left(\frac{\partial V}{\partial T}\right)_P = -\frac{RT}{(V - b)^2}\left(\frac{\partial V}{\partial T}\right)_P + \frac{R}{V - b}$$

$$\left(\frac{\partial V}{\partial T}\right)_P\left[\frac{RT}{(V-b)^2}-\frac{2a}{V^3}\right]=\frac{R}{V-b}$$

$$\left(\frac{\partial V}{\partial T}\right)_P=\frac{\frac{R}{V-b}}{\left[\frac{RT}{(V-b)^2}-\frac{2a}{V^3}\right]}$$

Substituting the value of $\left(\frac{\partial P}{\partial T}\right)_V$ and $\left(\frac{\partial V}{\partial T}\right)_P$ in equation (1) we have

$$C_P-C_V=T\frac{R}{V-b}\cdot\frac{\frac{R}{V-b}}{\left[\frac{RT}{(V-b)^2}\right]-\frac{2a}{V^3}}=\frac{\frac{R^2T}{(V-b)^2}}{\frac{RT}{(V-b)^2}\left[1-\frac{2a}{V^3}\frac{(V-b)^2}{RT}\right]}$$

So $$C_P-C_V=\frac{R}{1-\frac{2a}{V^3}\frac{(V-b)^2}{RT}}$$

Neglecting b in comparision to V $(V\gg b)\Rightarrow V-b\sim V$

$$C_P-C_V=\frac{R}{1-\frac{2a}{V^3}\frac{V^2}{RT}}=\frac{R}{1-\frac{2a}{RTV}}=R\left(1-\frac{2a}{RTV}\right)^{-1}$$

Expanding binomially and neglecting higher powers we get

$$C_P-C_V=R\left(1+\frac{2a}{RTV}\right)$$

**Q. From the first law of thermodynamics deduce**

(i) $dQ=C_VdT+\left[\left(\frac{\partial U}{\partial V}\right)_T+P\right]dV$ (ii) $C_P=C_V+\left[\left(\frac{\partial U}{\partial V}\right)_T+P\right]V\alpha$

(iii) $dQ=C_VdT+\frac{C_P-C_V}{V\beta}dV$

**Soln.** Consider a gaseous system whose thermodynamical state is described by any two of three variables (P, V & T)

Internal energy $U=f(T,V)$ ... (1)

According to Ist law of thermodynamics

$dQ=dU+dW$ ... (2)

where $dQ\rightarrow$ Amount of heat supplied to the system

$dU\rightarrow$ Change in the internal energy of the system

$dW\rightarrow$ Amount of work done by it.

If the change in the volume of the gas is dV then

$dW=PdV$ ... (3)

$\therefore$ $dQ=dU+PdV$ ... (4)

Since dU is a perfect differential

$$dU = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT \qquad \dots (5)$$

Now equation (4) become

$$dQ = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT + PdV$$

$$= \left(\frac{\partial U}{\partial T}\right)_V dT + \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right] dV \qquad \dots (6)$$

when we are considering the changes in which there is a change in the temperature of the system, the changes at constant temperature would automatically reduce to zero.

Two distinct cases arise.

(i) $V = \text{constant} \Rightarrow dV = 0$

Then $dQ = \left(\frac{\partial U}{\partial T}\right)_V dT$

Heat capacity at constant volume

$$C_V = \left(\frac{dQ}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V$$

Hence eqn (6) becomes

$$\boxed{dQ = C_V dT + \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right] dV} \qquad \dots (6(a))$$

(ii) Similarly, let $U = f(T, P)$ and $V = f(T, P)$

$dQ = dU + PdV$

$$\Rightarrow dQ = \left[\left(\frac{\partial U}{\partial P}\right)_T + P\left(\frac{\partial V}{\partial P}\right)_T\right] dP + \left[\left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P\right] dT \qquad \dots (7)$$

If $U = f(V, P)$ as independent variables

$$dQ = \left(\frac{\partial U}{\partial P}\right)_V dP + \left[\left(\frac{\partial U}{\partial V}\right)_P + P\right] dV \qquad (8)$$

When $P = \text{constant} \Rightarrow dP = 0$

So equation (7) become

$$dQ = \left[\left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P\right] dT$$

Hence heat capacity at constant pressure

$$C_P = \left(\frac{dQ}{dT}\right)_P = \left(\frac{\partial U}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P$$

But $\quad dU = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT$

So $\quad \left(\frac{\partial U}{\partial T}\right)_P = \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P + \left(\frac{\partial U}{\partial T}\right)_V$

$$C_P = \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P + \left(\frac{\partial U}{\partial T}\right)_V + P\left(\frac{\partial V}{\partial T}\right)_P = \left(\frac{\partial V}{\partial T}\right)_P \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right] + \left(\frac{\partial U}{\partial T}\right)_V$$

$$C_P = C_V + \left(\frac{\partial V}{\partial T}\right)_P \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right]$$

But coefficient of volume expansion is defined as

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \qquad \text{So} \quad \left(\frac{\partial V}{\partial T}\right)_P = V\alpha$$

$$\therefore \quad C_P = C_V + \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right] V\alpha \qquad \text{... (9)}$$

**(iii)** From equation (9)

$$\left(\frac{\partial U}{\partial V}\right)_T + P = \frac{C_P - C_V}{V\alpha}$$

Substituting this value in equation (6(a)) we get

$$\boxed{dQ = C_V dT + \frac{C_P - C_V}{V\alpha} dV} \qquad \text{... (10)}$$

**Q. For an ideal gas the molar heat capacity varies as $C = C_v + 3aT^2$. Find the equation of state for the process in the variables T and V where a is constant. $C_V$ is heat capacity at constant volume.**

**Soln.** $dQ = dU + dW \Rightarrow \quad CdT = C_v dT + PdV \Rightarrow (C_v + 3aT^2)dT = C_v dT + PdV$

$$\Rightarrow C_v dT + 3aT^2 dT = C_v dT + PdV \Rightarrow 3aT^2 dT = PdV \quad \Rightarrow 3aT^2 dT = \frac{nRT}{V} dV$$

$\Rightarrow 3a\int TdT = nR\int \frac{dV}{V} \qquad \Rightarrow 3a\frac{T^2}{2} = nR\ell n(V/A)$ where A is a constant of integration.

$$\Rightarrow \frac{3a}{2}\frac{T^2}{nR} = \ell n\left(\frac{V}{A}\right) \qquad \Rightarrow V = Ce^{+3aT^2/2nR}$$

or $\boxed{Ve^{-3aT^2/2nR} = \text{constant}}$

for an ideal gas $n = 1$

$$\boxed{Ve^{-3aT^2/2R} = \text{constant}}$$

**Q. Prove that the fall in temperature by the gas during the adiabatic expansion from pressure $P_1$ and $P_2$ at temperature T is given as**

$$dT = \frac{T}{C_P}\left(\frac{\partial V}{\partial T}\right)_P dP = \frac{TV\alpha}{C_P} dP$$

**Soln.** The work done for the adiabatic expansion of a gas is

$W = PdV \qquad \text{... (i)}$

From Ist law of thermodynamics $\rightarrow$ $dQ = dU + dW$

For adiabatic change $dQ = 0 \rightarrow dU = -dW = -PdV$

For 1 gm mole of the gas the change in internal energy for a change in temperature by dT is:

$$dU = C_V\, dT \quad \text{or} \quad dT = \frac{dU}{C_V} = -\frac{PdV}{C_V} \qquad \text{... (ii)}$$

For perfect gas under adiabatic process

$$PV^\gamma = K\,(\text{constant}) \quad \Rightarrow P\gamma V^{\gamma-1}dV + V^\gamma dP = 0$$

$$\Rightarrow \quad PdV = -\frac{V^\gamma dP}{\gamma V^{\gamma-1}} = -\frac{V}{\gamma}dP \qquad \text{... (iii)}$$

Now $PV = nRT$ for n mole of gas

$PdV + VdP = nRdT$

At constant pressure $dP = 0 \Rightarrow P\left(\frac{\partial V}{\partial T}\right)_P = nR$

Hence, $PT\left(\frac{\partial V}{\partial T}\right)_P = nRT \quad \Rightarrow PT\left(\frac{\partial V}{\partial T}\right)_P = PV \quad \text{or} \quad V = T\left(\frac{\partial V}{\partial T}\right)_P$

Substituting this value of V in equation (iii)

We get $PdV = -\frac{T}{\gamma}\left(\frac{\partial V}{\partial T}\right)_P dP$

From equation (ii) $\quad dT = -\frac{PdV}{C_V} = \frac{T}{C_V}\frac{1}{\gamma}\left(\frac{\partial V}{\partial T}\right)_P dP$ (using above equation)

Now $\gamma = \frac{C_P}{C_V}$

$$\therefore \quad \boxed{dT = \frac{T}{C_P}\left(\frac{\partial V}{\partial T}\right)_P dP} \qquad \text{... (iv)}$$

The volume expansion of gas

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \quad \text{or} \quad \left(\frac{\partial V}{\partial T}\right)_P = V\alpha$$

Hence

$$\boxed{dT = \frac{TV\alpha}{C_P}dP = \frac{T}{C_P}\left(\frac{\partial V}{\partial T}\right)_P dP}$$

**Q. If the degree of freedom of a gas is n, then find the ratio of $C_p$ and $C_v$.**

**Soln.** Molar specific heat $C_V = \frac{dU}{dT}$, $\quad C_V = \frac{d}{dT}\left(\frac{n}{2}RT\right) = \frac{n}{2}R$

$$C_p - C_v = R, \qquad C_p = R + C_v = R + \frac{n}{2}R = \left(1+\frac{n}{2}\right)R$$

$$\therefore \frac{C_p}{C_v} = \frac{\left(\frac{n}{2}+1\right)R}{\frac{n}{2}R} \Rightarrow \boxed{\frac{C_p}{C_v} = 1+\frac{2}{n}}.$$

**Q.** **Gas equation during an adiabatic process : Prove** $PV^{\gamma} = TV^{\gamma-1} = P^{\gamma-1}/T^{\gamma} = \text{constant}$

**Soln.** For adiabatic process, $dQ = 0$

$$dU + dW = 0 \Rightarrow nC_V dT + PdV = 0$$

$$\Rightarrow \quad nC_V \frac{dT}{T} + nRT\frac{dV}{V} = 0$$

$$\Rightarrow \quad nC_V \ln T + nR \ln V = 0$$

$$\Rightarrow \quad \frac{nR}{\gamma-1}\ln T + nR\ln V = 0$$

$$\Rightarrow \quad TV^{\gamma-1} = \text{constant}$$

Moreover, we have

$$\frac{PV}{nR}V^{\gamma-1} = \text{constant} \Rightarrow \quad PV^{\gamma} = \text{constant}$$

Futhermore, we have,

$$P\left(\frac{nRT}{P}\right)^{\gamma} = \text{constant} \Rightarrow \quad P^{1-\gamma}T^{\gamma} = \text{constant}$$

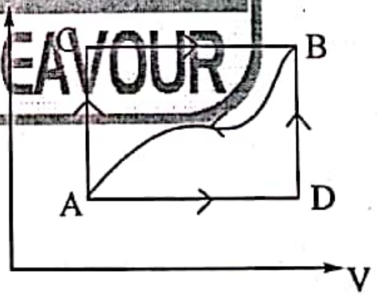
Or, $$\frac{P^{\gamma-1}}{T^{\gamma}} = \text{constant}$$

**Q.** **When a system is taken from the state A to the state B along the path ACB, 80 joule of heat flows into the system and the system does 30 joule of work.**

**(i) How much heat flows into the system along the path ADB if work done is 10 J ?**

**(ii)The system is returned from state B to state A along the curved path. The work done on the system is 20 joule. Does the system absorb or liberate heat and how much?**

**(iii) If $U_A = 0$, $U_D = 40$ J. Find the heat absorbed in the process AD & DB.**



**Soln.** (i) $W = 10J$

Heat along ADB

$dQ = dU + dW = 50 + 10 = 60$ Joule

$$\begin{cases} \because dQ = dU + dW \\ \Rightarrow dU = 80 - 30 = 50 \text{ Joule} \end{cases}$$

(ii) $dW = -20J$

$dQ = dU + dW$

$= 50 - 20 = 30$ Joule

Liberated heat $= 80 - 30 = 50$ Joule

(iii) $U_A = 0, \quad U_D = 40J$

for path DB, $\delta W = 0 \Rightarrow dQ = dU$

$(U_B - U_A) = 80J$

for path AD, $dU = U_D - U_A = 40J$

$$dQ = dU + dW = 40 + 10 = 50 \text{ joule} \quad \begin{cases} \text{for DB}, & dW = 0 \\ \text{for ADB}, & dW = 10J \end{cases}$$

**Q.** **A motor car tyre has a pressure of 2 atm at room temperature 27°C. If the tyre suddenly bursts. Find the resulting temperature.**

**Soln.** $P_1 = 2$ atm $\quad P_2 = 1$ atm

$T_1 = 27°C = 27 + 273 = 300$ K $\quad T_2 = ?$

$\gamma = 1.4$ for air

Formula $\frac{P_1^{\gamma-1}}{T_1^{\gamma}} = \frac{P_2^{\gamma-1}}{T_2^{\gamma}}$

$$\left(\frac{P_2}{P_1}\right)^{\gamma-1} = \left(\frac{T_2}{T_1}\right)^{\gamma}$$

$$\left(\frac{1}{2}\right)^{1.4-1} = \left(\frac{T_2}{300}\right)^{1.4} \Rightarrow \left(\frac{1}{2}\right)^{0.4} = \left(\frac{T_2}{300}\right)^{1.4}$$

$T_2 = 246.1$ K $= -26.9°C$

**Q.** **A quantity of air at 27°C and atmospheric pressure is suddenly compressed to half its original volume. Find the i) pressure and ii) temperature.**

**Soln.** Given $P_1 = 1$ atm $\quad P_2 = ? \quad \gamma = 1.4$

$V_1 = V \quad V_2 = V/2 \quad T_1 = 27°C = 300K \quad T_2 = ?$

$P_1V_1^{\gamma} = P_2V_2^{\gamma}$

$$P_2 = P_1\left(\frac{V_1}{V_2}\right)^{\gamma} = 1\left(\frac{V}{\frac{V}{2}}\right) = 1(2)^{1.4} = 2.636 \text{ atm}$$

$T_1V_1^{\gamma-1} = T_2V_2^{\gamma-1}$

$$T_2 = T_1\left(\frac{V_1}{V_2}\right)^{\gamma-1} = 300\left(\frac{V}{\frac{V}{2}}\right)^{1.4-1}$$

$$= 300\,(2)^{0.4} = 395.9\text{K} = 122.9°\text{C}$$

**Q.** **Air is compressed adiabatically of half its volume. Calculate the change in its temperature.**
Let the initial temperature be $T_1$ and final temperature $T_2$

**Soln.** Initial volume $V_1 = V$ and final volume $V_2 = \frac{V}{2}$

For adiabatic process $T_1V_1^{\gamma-1} = T_2V_2^{\gamma-1}$

$$T_2 = T_1\left(\frac{V_1}{V_2}\right)^{\gamma-1} \text{ or } T_2 = T_1\,(2)^{1.4-1}$$

$$\boxed{T_2 = [2]^{0.4}\,T_1 = 1.319T_1}$$

So change in temperture.

$$T_2 - T_1 = 1.319T_1 - T_1 = 0.319T_1$$

**Q.** **1 gm molecule of a monatomic $\left(\gamma=\frac{5}{3}\right)$ perfect gas at 27°C is adiabatically compressed in a reversible process from an initial pressure of 1 atmosphere to a final pressure of 50 atmosphere. Calculate the resulting difference in temperature.**

**Soln.** Given $P_1 = 1\text{ atm}$ $\quad P_2 = 50\text{ atm}$ $\quad T_1 = 27°C = 300K$

$T_2 = ?\quad \gamma = 5/3$

$$\frac{P_1^{\gamma-1}}{T_1^{r}} = \frac{P_2^{\gamma-1}}{T_2} \text{ or } \left(\frac{P_2}{P_1}\right)^{\gamma-1} = \left(\frac{T_2}{T_1}\right)^{\gamma}$$

$$(50)^{\frac{5}{3}-1} = \left(\frac{T_2}{300}\right)^{\frac{5}{3}} \Rightarrow 50^{\frac{2}{3}} = \left(\frac{T_2}{300}\right)^{\frac{5}{3}}$$

$$\frac{2}{3}\log 50 = \frac{5}{3}\log T_2 - \frac{5}{3}\log 30$$

$$T_2 = 1434\text{ K} = 1161°C$$

## Work done during an isothermal process

**Q.** **A certain gas obeys the eqn of state $P(V-b) = RT$**

**(i) Derive an expression for heat and work in a reversible isothermal expansion of the gas**

**(ii) Derive an expression for heat and work in a reversible adiabatic expansion of the gas**

**(iii) Calculate $\Delta U$, Q and W when 1 mol of the gas expands reversibly at 300K from 0.220 to 20.02 litre**

**(i) isothermally (ii) adiabatically. Assume that $b = 0.020$ lit mol$^{-1}$, $C_V = \frac{3}{2}R$ and $\gamma = \frac{5}{3}$**

**Soln.** (i) $dW = PdV$ $\quad$ or $W = \int_{V_1}^{V_2} PdV$

Given equation of state is $P = \frac{RT}{(V-b)}$

Thus $\quad W = \int_{V_1}^{V_2} \frac{RT}{V-b}dV = RT\ell n\left(\frac{V_2-b}{V_1-b}\right)$

Now, $dU = \left(\frac{\partial U}{\partial V}\right)dV + \left(\frac{\partial U}{\partial T}\right)dT \qquad \left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P = T\left(\frac{\partial\left(\frac{RT}{V-b}\right)}{\partial T}\right)_V - P$

$$= \frac{RT}{V-b} - P = P - P = 0 \qquad \because \Delta U = 0$$

Thus, $\quad \Delta Q = \Delta U - W = -W = RT\,\ell n\left(\frac{V_2-b}{V_1-b}\right)$

(ii) for adiabatic reversible expansion $\rightarrow Q = 0$

Hence $dU = -dW = -\frac{RT}{V-b}dV$

$$\Rightarrow \int_{T_1}^{T_2} \frac{C_V dT}{T} = -\int_{V_1}^{V_2} \frac{R}{V-b}dV \Rightarrow C_V \ell n\left(\frac{T_2}{T_1}\right) = -R\ell n\left(\frac{V_2-b}{V_1-b}\right)$$

$$\Rightarrow \frac{T_2}{T_1} = \left(\frac{V_2-b}{V_1-b}\right)^{-R/C_V} = \left(\frac{V_2-b}{V_1-b}\right)^{-(\gamma-1)}$$

$$\therefore \quad W = -\Delta U = -C_V(T_2 - T_1) = -C_V T_1 [\left(\frac{V_1-b}{V_2-b}\right)^{\gamma-1} - 1]$$

(iii) $T_1 = T_2 = 300K$, $V_1 = 0.220$ litre, $V_2 = 20.020$ litre, $b = 0.020$ litre

For isothermal reversible expansion

$$W = -\Delta Q = -RT_1 \ \ell n\left(\frac{V_2-b}{V_1-b}\right) = -(8.314)(300)\ell n\left(\frac{20.0}{0.20}\right) = -11.548 \text{ KJ mol}^{-1}$$

$\Delta U = 0$

Now, for an adiabatic reversible expansion

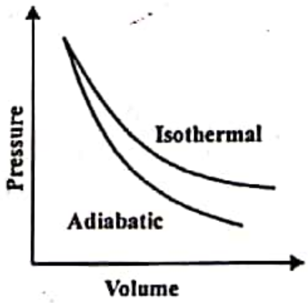
$\Delta Q = 0$

$$\Delta U = -W = -C_V T_1 \left[\left(\frac{V_1-b}{V_2-b}\right)^{\gamma-1} - 1\right]$$

Given $C_V = \frac{3}{2}R$, $\gamma = \frac{5}{3}$ and $T_1 = 300$ K

$$\Delta U = -W = -\left(\frac{3}{2}R\right)(300)\left[\left(\frac{200}{20000}\right)^{2/3} - 1\right] = 3.554 \text{ kJ.}$$

## Slope of Adiabatic and Isothermal Process



**(a) Isothermal Process :** For an ideal gas, we have

$$PV = \text{constant} \Rightarrow PdV + VdP = 0 \Rightarrow \left(\frac{dP}{dV}\right)_{iso} = -\frac{P}{V}$$

**(b) Adiabatic Process :** For an ideal gas, we have

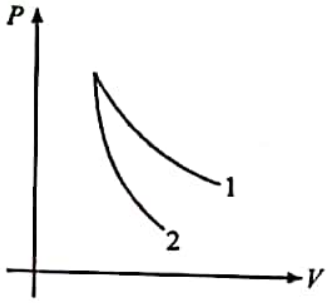
$$PV^{\gamma} = \text{Constant} \Rightarrow P\gamma V^{\gamma-1}dV + dP \cdot V^{\gamma} = 0 \Rightarrow \frac{dP}{dV} = -\frac{PV^{\gamma-1}\gamma}{V^{\gamma}}$$

$$\Rightarrow \left(\frac{dP}{dV}\right)_{adia} = -\gamma\frac{P}{V}$$

$$\therefore \quad \boxed{\frac{(dP/dV)_{adia.}}{(dP/dV)_{iso.}} = \gamma > 1} \quad \text{... (35)}$$

This shows that slope of adiabatic is γ-times than that of isothermal. Moreover, the adiabatic constant (γ) can also be defined as the ratio of slope of *P-V* curve for an adiabatic process to slope of *P-V* curve for an isothermal process.

**Q.** P-V plots for two gases during adiabatic processes are shown in the figure. Plots 1 and 2 should correspond respectively to



(a) He and $O_2$ (b) $O_2$ and He (c) He and Ar (d) $O_2$ and $N_2$

**Soln.** In adiabatic process, $PV^{\gamma} = \text{constant}$

Therefore, slope of P-V graph, $\frac{dP}{dV} = -\gamma \frac{P}{V}$

$\Rightarrow$ slope $\propto \gamma$ (with negative sign)

From the given graph, $(\text{slope})_2 > (\text{slope})_1$

$\therefore \ \gamma_2 > \gamma_1$

Therefore, 1 should correspond to $O_2$ $(\gamma = 1.4)$ and 2 should correspond to He $(\gamma = 1.67)$.

**Correct option is (b)**

**Q. If the eqn of state for a gas with internal energy U is $PV = \frac{1}{3}U$ then the equation for an adiabatic process is:**

(i) $PV^{1/3} = \text{constant}$ (ii) $PV^{2/3} = \text{constant}$

(iii) $PV^{4/3} = \text{constant}$ (iv) $PV^{3/5} = \text{constant}$

**Soln.** For adiabatic process $dQ = 0$

$dU = -dW = -PdV$

But $PV = \frac{1}{3}U \to U = 3PV$

$d(3PV) = -PdV = 3\,PdV + 3\,VdP = -PdV$

$3\,VdP = -4PdV$ or $\frac{dP}{P} = -\frac{4}{3}\frac{dV}{V}$.

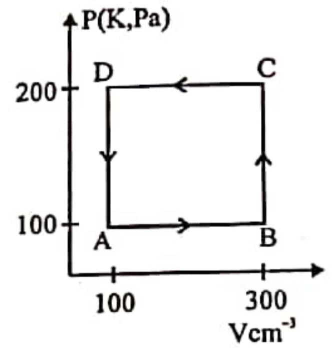
Integrating, $\log P = -\frac{4}{3}\log V + \log C$

$\log P + \log V^{4/3} = \log C \Rightarrow \log PV^{4/3} = \log C$ here C is a constant

$$\boxed{PV^{\frac{4}{3}} = \text{constant}}$$

**Option (iii) is correct**

**Q.** **A thermodynamic system is taken through the cycle ABCDA as shown in figure. (i) Calculate the work done by the gas (system) during the path AB, BC, CD, DA. (ii) Find the total heat rejected by the gas during the process ABCDA.**



**Soln.** (i) $W_1 = P\Delta V = 100\ \text{KPa} \times 200\ \text{cm}^{-3}$ (along AB)

$$= 100 \times 1000 \times \frac{200}{10^6} \frac{\text{Pa}}{\text{m}^3} = 20\ \text{J}$$

$W_2 = 0$ because the change in volume $= 0$ (along BC)

$W_3 = P \times \Delta V = -200\ \text{KP}_a \times 200\ \text{cm}^{-3} = -200 \times 1000 \times \frac{200}{10^6} \frac{\text{P}_a}{\text{m}^3} = -40\ \text{J}$ (along CD)

The negative sign is due to decrease in volume

$W_4 = 0$ (along DA)

$\therefore \quad W = W_1 + W_2 + W_3 + W_4 = 20 - 40 = -20\text{J}$

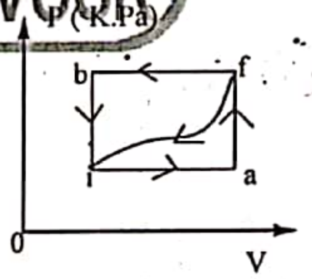
(ii) $dQ = dU + dW$

For cyclic process, $dU = 0$

$dQ = dW = -20\text{J} \rightarrow$ Heat rejected by the gas

**Q.** **When a system is taken from a state i to f along the path i a f as shown in figure. It is found that heat Q absorbed by the system is 50 cal and the work done by the system is 20 cal Along the path ibf Q = 36 cal**

**(i) What is the work done alone the path i bf ?**



**(ii) If the work done on the system is equal to 13 cal for the curved returned path fi. What is the value Q for this path ?**

**(iii) If U of the system in initial state is equal to 10 cal. What is the internal energy of the system in final state ?**

**(iv) If internal energy of the system for state B = 22 cal. What are the values Q for the process b f and i b?**

**Soln.** Given: $U_i = 10$ cal, $Q = 50$ cal, and $W = 20$ cal

for the path iaf

(i) $Q = U_f - U_i + W \Rightarrow 50 = U_f - 10 + 20$

$$\Rightarrow \quad \boxed{U_f = 40\ \text{cal}}$$

So work done along ibf

as $dQ = 36$

$dQ = dU + dW$

$\Rightarrow$ $dW = dQ - dU = 36 - (40-10) = \boxed{6 \text{ cal}}$

(ii) $W = 13$ cal for ( of → i), $W = -13$ cal, $dQ = dU + dW$

$= (U_i - U_f) - 13 = -30 - 13 = -43$ Cal

(iii) $\Delta U = 30$

$\Rightarrow U_f - U_i = 30$ $\Rightarrow U_f - 10 = 30 \Rightarrow \boxed{U_f = 40}$

(iv) $U_b = 22$ cal $U_i = 10$ cal

So for path b f $\Rightarrow U_f - U_i = 18$ cal

$\Rightarrow$ for b → $\Delta W = 0$

so $dQ = dU$

$\Rightarrow$ $\boxed{dQ = 18 \text{ cal}}$

For path i → b

$\Delta U = U_b - U_i = 12$

$dQ = \Delta U + dW$

As $\Delta w = 6$ {because for b → f $\Delta W = 0$

$dQ = 12 + 6 = 18$ cal

$\Rightarrow$ $\boxed{dQ = 18 \text{ cal}}$

**Q.** **An ideal gas expands adiabatically but quasistatically from state $i(P_i V_i T_i)$ to a state $f(P_f V_f T_f)$. What is the change in its internal energy? What would this change be if the expansion were isothermal?**

**Soln.** **Quasistatic process :** If the process is performed in such a way that at any instant during the process the system is very nearly in the thermodynamic equilibrium, the process is called quasistastic this means we can specify pressure, volume, temperature uniquely at any instant during such a process. Thus a quasistastic process is an idealised process in which all changes take place infinitely slowly from 1st law $dQ = dU + dW$

But for adiabatic process $dQ = 0$

So $dU = -dW$

Total change in internal energy $= \int_i^f dU = -\int_i^f P dV = -\int_i^f K/V^\gamma \, dV$

So $U_f - U_i = -K\left(\frac{V^{-\gamma+1}}{-\gamma+1}\right)_i^f$ $\left\{\begin{array}{l}\text{as } PV^\gamma = K \\ P = \dfrac{K}{V^\gamma}\end{array}\right.$

$= \frac{K}{1-\gamma}\left(V^{-\gamma+1}\right)_i^f$

But $P_i V_i^\gamma = P_f V_f^\gamma = K$

So $U_f - U_i = \frac{1}{1-\gamma}\left(P_f V_f^\gamma V_f^{-\gamma+1} - P_i V_i^\gamma V_i^{-\gamma+1}\right)$

$= \frac{1}{1-\gamma}(P_f V_f - P_i V_i)$ use $PV = RT$

$$\boxed{\Delta U = \frac{R}{1-\gamma}(T_f - T_i)}$$

(ii) for isothermal expansion $T_i = T_f$

$$U_f - U_i = \frac{R}{1-\gamma}(T-T) = 0$$

So for quasistatic isothermal process, the change in internal energy is Zero.

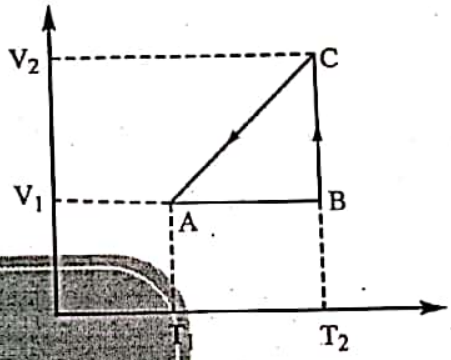
**Q.** **Figure shows a process ABCA performed on an ideal gas. Find the net heat given to the system during the process.**

**Soln.** Since the process is cyclic so the change in internal energy $dU = 0$

Since $dU = 0 \quad \Rightarrow \quad dQ = dW = PdV$

For the process AB change in volume = Zero

$$\Rightarrow W_1 = 0$$



For process BC → Temp is constant

$$W_2 = \int_{V_1}^{V_2} dW_2 = \int_{V_1}^{V_2} PdV = \int_{V_1}^{V_2} \frac{TR}{V} dV$$

$$W_2 = RT\ell n\, V\Big]_{V_1}^{V_2} = RT_2 \ell n \frac{V_2}{V_1}$$

For process $AC \rightarrow \frac{V}{T} = \text{constant}$

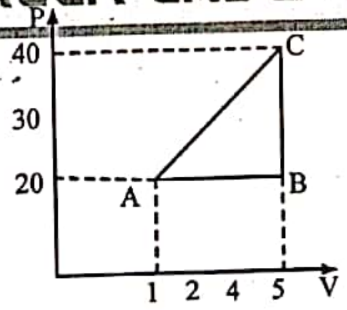
$$PV = RT \Rightarrow \frac{V}{T} = \frac{R}{P} \Rightarrow V = \frac{RT}{P} \Rightarrow dV = \frac{R}{P} dT$$

$$W_3 = \int_{T_2}^{T_1} dW = \int_{T_2}^{T_1} PdV = \int_{T_2}^{T_1} P\frac{R}{P} dT = [RT]_{T_2}^{T_1} = R(T_1 - T_2)$$

$$W_3 = R(T_1 - T_2)$$

Now $\quad Q = W = W_1 + W_2 + W_3 = R\left[T_2 \ell n \frac{V_2}{V_1} + (T_1 - T_2)\right]$

**Q.** **A gas is carried through a cycle ABCA as shown in the P–V diagram fig. Determine whether the heat is given to the system or by the system. Work done by the system or on the system. Internal energy of the system increases or decreases in the following process.**



**(i) For the process AB if $\Delta U = +Ve$**
**(ii) For the process BC if $Q = +Ve$**
**(iii) For process CA**
**(iv) For AB net work done in the complete cycle.**

**Soln.** (i) $\Delta U = +Ve$ (given) → so internal energy of the system increase

$\Delta W = +Ve$ (work done by the system because volume increase)

$\Delta Q = \Delta U + \Delta W = +Ve$ (Heat given to the system)

(ii) For BC

$Q = +Ve$ (given) → Heat given to the system

$\Delta W = 0$ ( because V = Const W = PV, dV = 0, So W = 0)

$\Delta U = +$ Ve $\Delta Q = \Delta U + \Delta W$. Internal energy of the system increase)

(iii) For process CA

For process ABC $\Delta U = +Ve \left(\because (\Delta U)_{AC} = (\Delta U)_{AB} + (\Delta U)_{BC} = +Ve\ +\ +Ve\right.$

For CA Process $(\Delta U)_{CA} = -(\Delta U)AC = -Ve$

$(\Delta U)_{CA} = -ve$ ( Internal energy of the system decrease)

$\Delta W = -ve$ ($\because$ volume decrease so workdone on the system)

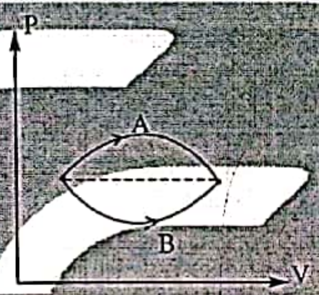
$\Delta Q = -ve$ ($\Delta Q = \Delta U + \Delta W = -ve$, heat is given by the system)

(iv) Net workdone in couple cycle = area under the curve

$$= \frac{1}{2} \times AB \times BC = \tfrac{1}{2} \times 3 \times 20 = 30 \text{ Joule.}$$

**Q.** **Fig shows the process A and B on a system. Let $\Delta Q_1$ and $\Delta Q_2$ be the heat given to the system in the process A and B respectively. Then,**

**(i)** $\Delta Q_1 > \Delta Q_2$ **(ii)** $\Delta Q_1 = \Delta Q_2$ **(iii)** $\Delta W$ **(iv)** $\Delta Q_1 \le \Delta Q_2$



**Soln.** Since $\Delta U$ is same for both the process and $\Delta W$ is the amount of work which is represented by the area under the curve.

$\Delta Q = \Delta U + \Delta W \rightarrow \Delta Q$ will vary as $\Delta W$

Since area under A is greater than area under B

$\Rightarrow \Delta W_A > W_B$, so $\Delta Q_1 > \Delta Q_2$

If both the arrow signs are changed then

$\Delta Q_1 < \Delta Q_2$

**Q.** **P, V and T for a certain gas are related by $P = \dfrac{\alpha T - \beta T^2}{V}$, where $\alpha$ and $\beta$ are constants. Find the workdone by the gas if the temperature changes from $T_1$ to $T_2$ while pressure remains constant.**

**Soln.** PV = RT $\Rightarrow$ PdV = RdT, ($\because$ Pressure is constant)

$$\Rightarrow dV = \frac{RdT}{P}$$

So, $dW = PdV = \alpha T - \beta T^2 \Rightarrow dW = \alpha dT - 2\beta T dT$,

$$\Rightarrow W = \alpha \int_{T_1}^{T_2} (\alpha dT - 2\beta T dT) \Rightarrow \quad W = \alpha(T_2 - T_1) - \beta(T_2^2 - T_1^2)\cdot$$

## Reversible and Irreversible processes

**Reversible Process :** A reversible process is one which can be reversed in such a way that all changes taking place in the direct process are exactly repeated in the opposite order and sense and no changes are left in any of the bodies taking part in the process or in the sorrounding.

**The condition for reversibility :**

A process can be reversible only when it satisfy two condition.

(i) Process must be quasistatic (If the process is performed in such a way that at any instant during the process the system is very nearly in the thermodynamic equilibrium)

A quasistatic process is an idealised process in which all changes take place infinitely slowly.

(ii) Process must be non-dissipiative (dissipiative force such as friction, resistance, Hysteresis etc must be completely absent).

**Q.** **Classify the reversible & irreversible process among the following:**

**Soln.** (1) Isothermal expansion of a gas → irreversible

(2) Isothermal quasistatic expansion of a gas → Reversible

(3) Adiabatic expansion of a gas → Irreversible

(4) Diffusion of a gas → irreversible

(5) Transfer of heat from hot body to cold body → irreversible

(6) Free expansion of a perfect gas → irreversible

(7) Transfer of heat by radiation → irreversible

(8) Electrical heating of wire → irreversible

(9) Very slow expansion or contraction of a spring → Reversible.

**Q.** An ideal gas expands in a process in which its pressure depends on the volume as $p = p_0 e^{-\alpha V}$, where $p_0$ and $\alpha$ are two positive constants. If n is the number of moles in the gas, the maximum temperature that it will attain in this process is (R is the universal gas constant)

(a) $p_0 / e\alpha nR$ (b) $p_0 / \alpha n^3 R$ (c) $ep_0^2 / \alpha nR$ (d) $p_0^2 / \alpha nR$

**Soln.** For an ideal gas, we have

$$PV = nRT \text{ or } T = \frac{PV}{nR} = \frac{P_0 V}{nR} e^{-\alpha V}$$

For temperature to be maximum, we have

$$\frac{dT}{dV} = 0$$

$$\Rightarrow \quad \frac{P_0 V}{nR}(-\alpha)e^{-\alpha V} + \frac{P_0}{nR}e^{-\alpha V} = 0$$

$$\Rightarrow \quad 1 - V\alpha = 0 \quad \Rightarrow \quad V\alpha = 1$$

$$\Rightarrow \quad V = \frac{1}{\alpha}$$

$$\therefore \quad T_{\max} = \frac{P_0 . \frac{1}{\alpha}}{nR} e^{-\alpha . \frac{1}{\alpha}} = \frac{P_0}{e\alpha nR}$$

**Correct option is (a)**

**Q.** In the temperature range 100 – 1000 °C, the molar specific heat of a metal varies with temperature $T$ (measured in degrees Celsius) according to the formula $C_p = (1 + T/5)$ J-deg $C^{-1}$ mol$^{-1}$. If 0.2 kg of the metal at 600 °C is brought in thermal contact with 0.1 kg of the same metal at 300 °C, the final equilibrium temperature, in deg C, will be
[Assume that no heat is lost due to radiation and/or other effects]. **[TIFR 2016]**

(a) 466 (b) 567 (c) 383 (d) 519

**Soln.**

| | |
|---|---|
| $M_1 = 0.2$ kg | $M_2 = 0.1$ kg |
| $T_1 = 600$ °C | $T_2 = 300$ °C |
| $= 873$ K | $= 573$ K |

Using the principle of calorimetry
Heat loss = Heat gain

We have, $-\left(\int dQ\right)_{\text{loss}} = \left(\int dQ\right)_{\text{gain}} \Rightarrow \int_{T_1}^{T_f} M_1 C_{p_1} dT = \int_{T_2}^{T_f} M_2 C_{p_2} dT$

where $T_f$ is the final equilibrium temperature.

$$\Rightarrow \quad -0.2\int_{T_1}^{T_f}\left(1+\frac{T}{5}\right)dT = 0.1\int_{T_2}^{T_f}\left(1+\frac{T}{5}\right)dT$$

$$\Rightarrow \quad -2\left[T+\frac{T^2}{10}\right]_{873}^{T_f} = \left[T+\frac{T^2}{10}\right]_{573}^{T_f}$$

$$\Rightarrow \quad -2\left(T_f+\frac{T_f^2}{10}\right)+2\left(873+\frac{873^2}{10}\right) = \left(T_f+\frac{T_f^2}{10}\right)-\left(573+\frac{573^2}{10}\right)$$

$$\Rightarrow \quad 3\left(T_f+\frac{T_f^2}{10}\right) = 2\left(873+\frac{873^2}{10}\right)+\left(573+\frac{573^2}{10}\right)$$

$$\Rightarrow \quad T_f^2 + 10T_f - 625259 = 0$$

$$\Rightarrow \quad T_f = \frac{-10 \pm \sqrt{10^2 + 4\times 625259}}{2} = 785.7\text{ K}, -795.7\text{ K (not admirable)}$$

So, $T_f = 785.7\text{ K} = 512.7$ °C.
The nearest answer is (d)
**Correct option is (d)**

**Q.** A monatomic gas is described by the equation of state $p(V - bn) = nRT$ where $b$ and $R$ are constants and other quantities have their usual meanings. The maximum density (in moles per unit volume) to which this gas can be compressed is **[TIFR 2013]**

(a) $\frac{1}{bn}$ (b) $b$ (c) $\frac{1}{b}$ (d) infinity

**Soln.** Given : $p(V - bn) = nRT$

$$\Rightarrow \quad \frac{nRT}{V} = p\left(1-\frac{bn}{V}\right)$$

Taking $\frac{n}{V} = \rho$ (the density), we have

$$RT\rho = p(1-b\rho) \text{ or } \rho = \frac{p}{pb+RT}.$$

For maximum density, we have $\frac{d\rho}{dp} = 0$

$$\frac{(pb+RT)-pb}{(pb+RT)} = 0 \Rightarrow T = 0$$

Therefore, $\rho_{\max} = \rho|_{T=0} = \frac{p}{pb} = \frac{1}{b}$.

**Correct option is (c)**

**Q.** An ideal diatomic gas is initially at a temperature $T = 0°C$. Then it expands reversibly and adiabatically to 5 times its volume. Its final temperature will be approximately **[TIFR 2015]**

(a) –180°C (b) –150°C (c) –130°C (d) 0°C

**Soln.** For adiabatic process of ideal gas, we have

$$T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}, \text{ where } T_1 = 273\text{ K}, V_2 = 5V_1, \gamma = \frac{7}{5} \text{ (for diatomic gas)}$$

Therefore, $T_2 = 273\left(\frac{V_1}{5V_1}\right)^{\frac{7}{5}-1} = \frac{273}{5^{2/5}} = 143.4\text{ K} = -129.59\text{ °C} \simeq -130\text{ °C}.$

**Correct option is (c)**

**Q.** A car tyre is slowly pumped up to a pressure of 2 atmospheres in an environment at 15°C. At this point, it bursts. Assuming the sudden expansion of the air (a mixture of $O_2$ and $N_2$) that was inside the tyre to be adiabatic, its temperature after the burst is **[TIFR 2010]**

(a) –55°C (b) –37°C (c) –26°C (d) +9°C

**Soln.** For adiabatic expansion, we have

$$P^{1-\gamma}T^{\gamma} = \text{constant or } TP^{(1-\gamma)/\gamma} = \text{constant or } T_1P_1^{(1-\gamma)/\gamma} = T_2P_2^{(1-\gamma)/\gamma}, \text{ where}$$

$$T_1 = 288\text{ K} \; ; \; P_1 = 2\text{ atm}$$

$$T_2 = ? \; ; \; P_2 = 1\text{ atm}$$

$$\Rightarrow \quad T_2 = 288\left(\frac{2}{1}\right)^{(1-\gamma)/\gamma}, \text{ where } \gamma = 1.4 \text{ (for air).}$$

$$\therefore \quad T_2 = 288(2)^{-2/7} = 236.25\text{ K} = -36.7\text{ °C}.$$

**Correct option is (b)**

**Q.** A thermally-insulated container of volume $V_0$ is divided into two equal halves by a non-permeable partition. A real gas with equation of state. **[TIFR 2014]**

$$b^3\left(p+\frac{a^2}{V^3}\right) = nRT$$

where 'a' and 'b' are constants, is confined to one of these halves at a temperature $T_0$. The partition is now removed suddenly and the gas is allowed to expand to fill the entire container. The final temperature of the gas, in terms of its specific heat $C_V$, will be

(a) $T_0 - \frac{3a^2}{2C_V V_0^2}$ (b) $T_0 - \frac{2a^2}{3C_V V_0^2}$ (c) $T_0 + \frac{3a^2}{2C_V V_0^2}$ (d) $T_0 + \frac{2a^2}{3C_V V_0^2}$

**Soln.** For free expansion, we have $dU = 0$, where $U = U(T, V)$.

So, $\left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV = 0$, where $\left(\frac{\partial U}{\partial T}\right)_V = C_v$

and $\boxed{\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P} = T\left(\frac{nR}{b^3}\right) - \left(\frac{nRT}{b^3} - \frac{a^2}{V^3}\right) = \frac{a^2}{V^3}$

$\therefore \quad C_v dT + \frac{a^2}{V^3} dV = 0 \qquad \Rightarrow \quad C_v \int_{T_0}^{T_f} dT + a^2 \int_{V_0/2}^{V_0} dV = 0$

$\Rightarrow \quad C_v(T_f - T_0) + \frac{3}{2}\frac{a^2}{V_0^2} = 0 \qquad \Rightarrow \quad T_f = T_0 - \frac{3}{2}\frac{a^2}{C_v V_0^2}$

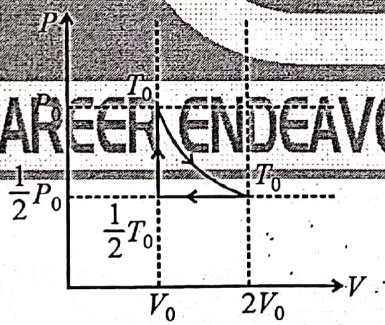
**Correct option is (a)**

**Q.** One mole of monoatomic ideal gas is initially at pressure $P_0$ and volume $V_0$. The gas then undergoes a three-stage cycle consisting of the following processes: **[TIFR 2017]**

(i) An isothermal expansion till it reaches volume $2V_0$, and heat $Q$ flows into the gas

(ii) An isobaric compression back to the original volume $V_0$

(iii) An isochoric increase in pressure till the original pressure $P_0$ is regained



**The corresponding P-V diagram is shown above**

The efficiency of this cycle can be expressed as

(a) $\varepsilon = \frac{4Q + 2RT_0}{4Q + RT_0}$ (b) $\varepsilon = \frac{4Q + 2RT_0}{4Q - 3RT_0}$ (c) $\varepsilon = \frac{4Q - 2RT_0}{4Q + RT_0}$ (d) $\varepsilon = \frac{4Q - 2RT_0}{4Q + 3RT_0}$

**Soln.** (i) For isothermal process,

The amount of work done is $W_1 = Q$.

This is positive as the gas is expanding in this process.

(ii) For isobaric process,

The amount of work done is

$$W_2 = \frac{P_0}{2}(V_0 - 2V_0) = -\frac{P_0 V_0}{2} = -\frac{RT_0}{2},$$

and the amount of heat exchanged is

$$\Delta Q_2 = nC_p\,\Delta T = \frac{5}{2}R\left(\frac{T_0}{2} - T_0\right) = -\frac{5RT_0}{4}.$$

Since $\Delta Q_2 < 0$, this amount of heat flows out of the system.

(iii) For isochoric process,

The amount of work done is $W_3 = 0$, and the amount of heat exchanged is

$$\Delta Q_3 = nC_v\,\Delta T = \frac{3}{2}R\left(T_0 - \frac{T_0}{2}\right) = \frac{3RT_0}{4}.$$

This amount of heat $\Delta Q_3$ being positive enters into the system.

Therefore, $\eta = \dfrac{\text{Total work done}}{\text{Heat input}}$

$$= \frac{Q - \frac{RT_0}{2}}{Q + \frac{3RT_0}{4}} = \frac{4Q - 2RT_0}{4Q + 3RT_0}$$

**Correct option is (d)**

**Q.** A thermally isolated container stores $N_2$ gas at 27.24 °C at one atmospheric pressure. Suddenly the pressure of the gas is increased to two atmospheric pressures. Assuming $N_2$ to behave as an ideal gas, estimate the change in temperature of the gas, in Celsius degree (°C). **[TIFR 2017]**

**Soln.** Since the pressure of the gas is suddenly increased, the process must be adiabatic. Hence, we have

$$P_1^{1-\gamma}T_2^{\gamma} = P_2^{1-\gamma}T_2^{\gamma}$$

$$\Rightarrow \quad T_2 = \left(\frac{P_1}{P_2}\right)^{1-\gamma/\gamma} T_1, \text{ where } \gamma = \frac{7}{5} \text{ for } N_2 \text{ gas}$$

$$\therefore \quad T_2 = \left(\frac{1}{2}\right)^{-2/7} \times 300.24 = 366\,K = 93\,°C$$

Therefore, change in temperature $= 93.00 - 27.24$

$= 65.76$

$\simeq 66$ °C

**Correct answer is (66)**

## PREVIOUS YEARS SOLUTIONS OF JEST

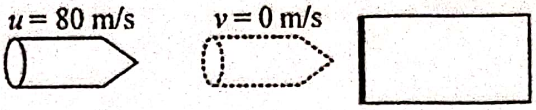
**Q.** A metal bullet comes to rest after hitting its target with a velocity of 80 m/s. If 50% of the heat generated remains in the bullet, what is the increase in its temperature? (The specific heat of the bullet = 160 Joule per Kg per degree. C) **[JEST 2013]**

(a) 14° C (b) 12.5° C (c) 10° C (d) 8.2° C

**Soln.** If $u$ and $v$ be the final velocity of the bullet then, the change in the bullet's energy is

$$\Delta K = \frac{1}{2}m(v)^2 - \frac{1}{2}m(u)^2 = -\frac{m}{2}(80)^2,$$

where $m$ is the mass of the bullet.



If 50% of this energy remains in the bullet in the form of heat, then

$$50\% \text{ of } \frac{m}{2}(80)^2 = ms\Delta T$$

where '$s$' is the specific heat of the bullet.

Therefore, $\Delta T = \frac{1}{4} \times \frac{(80)^2}{160}$ $\qquad \left[\because s = 160 \text{ Jkg}^{-1}\,°\text{C}^{-1}\right]$

$= 10\,°\text{C}.$

**Correct option is (a)**

**Q.** In a thermodynamic process, the volume of one mole of an ideal is varied as $V = aT^{-1}$, where $a$ is a constant. The adiabatic exponent of the gas is $\gamma$. What is the amount of heat received by the gas if the temperature of the gas increases $\Delta T$ in the process? **[JEST 2018]**

(a) $R\Delta T$ (b) $\frac{R\Delta T}{1-\gamma}$ (c) $\frac{R\Delta T}{2-\gamma}$ (d) $R\Delta T\frac{2-\gamma}{\gamma-1}$

**Soln.** Given : $V = aT^{-1} = \frac{a}{T}$

From first law of thermodynamics,

$$dQ = dU + PdV \quad \text{where, } dU = \frac{f}{2}nRdT \text{ (for an ideal gas)}$$

$$\therefore \quad dQ = \frac{f}{2}nRdT + \frac{nRT}{V}dV$$

$$= \frac{f}{2}nRdT + \frac{nRT}{a/T}\left(\frac{-a}{T^2}\right)dT = \frac{f}{2}nRdT - nRdT = \left(\frac{f}{2}-1\right)nRdT$$

For 1 mole,

$$dQ = \left(\frac{f}{2}-1\right)RdT$$

$$\therefore \quad \Delta Q = \left(\frac{f}{2}-1\right)R\Delta T \quad \text{where, } \gamma = 1+\frac{2}{f} \text{ or } \frac{f}{2} = \frac{1}{\gamma-1}$$

$$\therefore \quad \Delta Q = \left(\frac{1}{\gamma-1}-1\right)R\Delta T = R\Delta T\left(\frac{2-\gamma}{\gamma-1}\right)$$

**Correct option is (d)**

**Q.** For a diatomic ideal gas near room temperature, what fraction of the heat supplied is available for external work if the gas is expanded at constant pressure? **[JEST 2013]**

(a) 1/7 (b) 5/7 (c) 3/4 (d) 2/7

**Soln.** From first law of thermodynamics, $dQ = dU + PdV$.

Therefore, $\left(\frac{dW}{dQ}\right) = \frac{PdV}{dU + PdV} = \frac{nR\,dT}{\frac{f}{2}nR\,dT + nR\,dT} = \frac{2}{f+2}$.

where $PdV = nR\,dT$ (at constant pressure), and $f = 5$ (for diatomic gas).

Therefore, $\frac{dW}{dQ} = \frac{2}{7}$.

**Correct option is (d)**

**Q.** A monoatomic ideal gas at 17°C is adiabatically compressed to 1/8 of its original volume. The temperature after compression is **[JEST 2012]**

(a) 2.1°C (b) 17°C (c) –200.5°C (d) 887°C

**Soln.** For adiabatic process, we have

$TV^{\gamma-1} =$ constant.

So, $T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}$

$$\Rightarrow T_2 = T_1\left(\frac{V_1}{V_2}\right)^{\gamma-1}, \text{ where } T_1 = 17\,^\circ\text{C} = 290\text{ K},\ V_2 = \frac{1}{8}V_1,\ \gamma = \frac{5}{3} \text{ (for monatomic gases)}$$

$$\text{Therefore, } T_2 = 290\left(\frac{V_1}{V_1/8}\right)^{2/3} = 290(2)^2 = 1160\text{ K} = 887\,^\circ\text{C}.$$

**Correct option is (d)**

**Q.** After the detonation of an atom bomb, the spherical ball of gas was found to be 15 meter radius at a temperature of $3\times10^5$ K. Given the adiabatic expansion coefficient $\gamma = \frac{5}{3}$, what will be the radius of the ball when its temperature reduces to $3\times10^3$ K? **[JEST 2017]**

(a) 156 m (b) 50 m (c) 150 m (d) 100 m

**Soln.** For adiabatic process, we have

$$T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}$$

where $V = \frac{4}{3}\pi r^3$

$$\therefore \quad T_1 r_1^{3(\gamma-1)} = T_2 r_2^{3(\gamma-1)}$$

$$\Rightarrow \quad r_2 = \left(\frac{T_1}{T_2}\right)^{1/3(\gamma-1)} r_1$$

$$\Rightarrow \quad r_2 = \left(\frac{3\times10^5}{3\times10^3}\right)\times 15 = 150\text{ m}.$$

**Correct option is (c)**

**Q.** An ideal gas is compressed adiabatically from an initial volume $V$ to a final volume $\alpha V$ and a work $W$ is done on the system in doing so. The final pressure of the gas will be $\left(\gamma = \frac{C_P}{C_V}\right)$, **[JEST 2015]**

(a) $\frac{W}{V^\gamma}\frac{1-\gamma}{\alpha-\alpha^\gamma}$ (b) $\frac{W}{V^\gamma}\frac{\gamma-1}{\alpha-\alpha^\gamma}$ (c) $\frac{W}{V}\frac{1-\gamma}{\alpha-\alpha^\gamma}$ (d) $\frac{W}{V}\frac{\gamma-1}{\alpha-\alpha^\gamma}$

**Soln.** For adiabatic process, $P_1 V_1^\gamma = P_2 V_2^\gamma$, where $V_1 = V$ and $V_2 = \alpha V$.

Therefore, $P_1V^{\gamma} = P_2(\alpha V)^{\gamma} \Rightarrow P_1 = P_2\alpha^{\gamma}$

Also, the work done for an adiabatic process is

$$\text{Work} = \frac{1}{\gamma-1}(P_1V_1 - P_2V_2)$$

$$\Rightarrow -W = \frac{1}{\gamma-1}(P_2\alpha^{\gamma}V - P_2\alpha V)$$

$\Rightarrow \frac{(1-\gamma)W}{V(\alpha^{\gamma}-\alpha)} = P_2 = \frac{(\gamma-1)W}{V(\alpha-\alpha^{\gamma})}.$

$$\Rightarrow P_2 = -\frac{W(\gamma-1)}{(\alpha^{\gamma}-\alpha)V} = \frac{W}{V}\frac{\gamma-1}{\alpha-\alpha^{\gamma}}.$$

**Correct option is (d)**

**Q.** A theoretical model for a real (non-ideal) gas gives the following expressions for the internal energy (U) and the pressure (P), $U(T,V) = aV^{-2/3} + bV^{2/3}T^2$ and $P(T,V) = \frac{2}{3}aV^{-5/3} + \frac{2}{3}bV^{-1/3}T^2$, where $a$ and $b$ are constants. Let $V_0$ and $T_0$ be the initial volume and initial temperature respectively. If the gas expands adiabatically, the volume of the gas is proportional to **[JEST 2018]**

(a) $T$ (b) $T^{3/2}$ [✓ (c) $T^{-3/2}$] (d) $T^{2}$

**Soln.** Given : $U(T,V) = aV^{-2/3} + bV^{2/3}T^2$ and $P(T,V) = \frac{2}{3}aV^{-5/3} + \frac{2}{3}bV^{-1/3}T^2$

For adiabatic process, $dU + PdV = 0$

$$\Rightarrow -\frac{2}{3}aV^{-5/3}dV + \frac{2}{3}bV^{-1/3}T^2dV + 2bV^{2/3}TdT + \frac{2}{3}aV^{-5/3}dV + \frac{2}{3}bV^{-1/3}T^2dV = 0$$

$$\Rightarrow \frac{4}{3}bV^{-1/3}T^2dV + 2bV^{2/3}TdT = 0$$

$$\Rightarrow \frac{2}{3}V^{-1}dV + \frac{dT}{T} = 0$$

Integrating, we have

$$\frac{2}{3}\ln V + \ln T = \text{constant}$$

$$\Rightarrow VT^{3/2} = \text{constant} \Rightarrow V \propto T^{-3/2}$$

**Correct option is (c)**

**Q.** An ideal gas has a specific heat ratio $C_P/C_V = 2$. Starting at a temperature $T_1$ the gas under goes an isothermal compression to increase its density by a factor of two. After this an adiabatic compression increases its pressure by a factor of two. The temperature of the gas at the end of the second process would be:

(a) $\frac{T_1}{2}$ [✓ (b) $\sqrt{2}T_1$] (c) $2T_1$ (d) $\frac{T_1}{\sqrt{2}}$ **[JEST 2016]**

**Soln.** Since $\frac{C_P}{C_V} = 2$, so $\gamma = 2$

For isothermal process,

$PV =$ constant, where density, $\rho = \frac{n}{V}$.

So, $\dfrac{P}{\rho}$ = constant.

Therefore, the pressure also gets doubled when the density gets doubled.

Now, for an adiabatic process, $T_1 P_1^{\frac{1}{\gamma}-1} = T_2 P_2^{\frac{1}{\gamma}-1}$, where $P_1 = 2P$ and $P_2 = 2P_1 = 4P$.

Therefore, $T_1 (2P)^{-1/2} = T_2 (4P)^{-1/2}$ $\quad [\because \gamma = 2]$

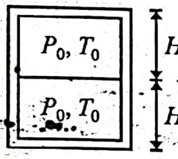
$\Rightarrow \quad T_2 = \sqrt{2}\, T_1$.

**Correct option is (b)**

**Q.** A frictionless, heat conducting piston of negligible mass and the heat capacity divides a vertical, insulated cylinder of height 2H and cross-sectional area A into two halves. Each half contains one mole of an ideal gas at temperature $T_0$ and pressure $P_0$ corresponding to STP. The heat capacity ratio $\gamma = C_p / C_v$ is given. A load of weight W is tied to the piston and suddenly released. After the system comes to equilibrium, the piston is at rest and the temperature of the gases in the two compartments are equal. What is the final displacement y of the piston from its initial, assuming $yW >> T_0 C_v$? **[JEST 2018]**

(a) $\dfrac{2H}{\sqrt{\gamma}}$ (b) $H\gamma$ (c) $\dfrac{H}{\sqrt{\gamma}}$ (d) $\dfrac{2H}{\gamma}$

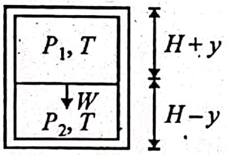
**Soln.** Initial condition :



The ideal gas equation gives

$$P_0 AH = RT_0$$

Final condition :



The ideal gas equation gives

$$P_1 A(H+y) = RT \quad \text{and} \quad P_2 A(H-y) = RT$$

The condition for equilibrium of piston gives

$$P_1 + \frac{W}{A} = P_2$$

$$\Rightarrow \quad \frac{RT}{A(H+y)} + \frac{W}{A} = \frac{RT}{A(H-y)}$$

$$\Rightarrow \quad \frac{2RTy}{H^2 - y^2} = W$$

Moreover, the first law of thermodynamics gives

$$dU_1 + dU_2 - Wy = 0$$

$\Rightarrow \quad nC_V(T-T_0)+nC_V(T-T_0)=Wy$

$\Rightarrow \quad 2nC_VT=Wy$, where $Wy \gg T_0C_V$

$$\Rightarrow \quad W=\frac{2nC_VT}{y}$$

$$\Rightarrow \quad \frac{2RTy}{H^2-y^2}=\frac{2RT}{(\gamma-1)y} \Rightarrow y=\frac{H}{\sqrt{\gamma}}$$

**Correct option is (c)**

**Q.** In an experiment, certain quantity of an ideal gas at temperature $T_0$, pressure $P_0$ and volume $V_0$ is heated by a current flowing through a wire for a duration of $t$ seconds. The volume is kept constant and the pressure changes to $P_1$. If the experiment is performed at constant pressure starting with the same initial conditions, the volume changes from $V_0$ to $V_1$. The ratio of the specific heats at constant pressure and constant volume is

(a) $\frac{P_1-P_0}{V_1-V_0}\frac{V_0}{P_0}$ (b) $\frac{P_1-P_0}{V_1-V_0}\frac{V_1}{P_1}$ (c) $\frac{P_1V_1}{P_0V_0}$ (d) $\frac{P_0V_0}{P_1V_1}$ **[JEST 2018]**

**Soln.** If the volume is kept constant

$$dQ_1=dU=\frac{f}{2}nRdT=\frac{f}{2}(VdP)$$

$$\therefore \quad \Delta Q_V=\frac{f}{2}V_0(P_1-P_0)$$

If the pressure is constant,

$$dQ_P=nC_PdT=\left(\frac{f}{2}+1\right)nRdT=\left(\frac{f}{2}+1\right)(PdV)$$

$$\therefore \quad \Delta Q_P=\left(\frac{f}{2}+1\right)P_0(V_1-V_0)$$

If both the processes are same, the same amount of heat flows. So,

$$\Delta Q_V=\Delta Q_P$$

$$\Rightarrow \quad \frac{f}{2}V_0(P_1-P_0)=\left(\frac{f}{2}+1\right)P_0(V_1-V_0)$$

$$\Rightarrow \quad 1+\frac{2}{f}=\frac{V_0(P_1-P_0)}{P_0(V_1-V_0)} \quad where,\ 1+\frac{2}{f}=\gamma$$

$$\therefore \quad \gamma=\frac{P_1-P_0}{V_1-V_0}\frac{V_0}{P_0}$$

**Correct option is (a)**

**Q.** An ideal fluid is subjected to a thermodynamic process described by $\rho=CV^{-\alpha}$ and $P=n\rho^{\Gamma}$, where $\rho$ is energy density and P is pressure. For what values of $n$ and $\Gamma$, the process is adiabatic if the volume is changed slowly? **[JEST 2018]**

(a) $\Gamma=\alpha-1, n=1$ (b) $\Gamma=1-\alpha, n=\alpha$ (c) $\Gamma=1, n=\alpha-1$ (d) $\Gamma=\alpha, n=1-\alpha$

**Soln.** Given: $\rho=\frac{U}{V}=CV^{-\alpha}$ $or$ $U=CV^{-\alpha+1}$

And $$P = n\rho^{\Gamma} = n\left(\frac{U}{V}\right)^{\Gamma} = n\left(CV^{-\alpha}\right)^{\Gamma}$$

From first law of thermodynamics, we have

$$dQ = dU + PdV$$

For adiabatic process, we have

$$dQ = 0$$

$$\Rightarrow \quad dU + PdV = 0$$

$$\Rightarrow \quad d\left(CV^{-\alpha+1}\right) + nC^{\Gamma}V^{-\alpha\Gamma}dV = 0$$

$$\Rightarrow \quad C(-\alpha+1)V^{-\alpha}dV + nC^{\Gamma}V^{-\alpha\Gamma}dV = 0$$

$$\Rightarrow \quad C(1-\alpha)V^{-\alpha} = -nC^{\Gamma}V^{-\alpha\Gamma}$$

$$\Rightarrow \quad (\alpha-1) = nC^{\Gamma-1}V^{-\alpha(\Gamma-1)}$$

On comparing, we have

$$n = \alpha - 1 \text{ and } \Gamma - 1 = 0$$

Or, $$n = \alpha - 1 \text{ and } \Gamma = 1$$

**Correct option is (c)**

# Chapter 3

# Laws of thermodynamics & their Consequences-2

## Second law of Thermodynamics

The 1st law of thermodynamics tells that energy of the universe remain constant. This law tell us that heat and mechanical work both are interconvertible. It doesn't tell us the limitation and condition for this conversion i.e how much heat is converted into work and weather the transformation itself can take place or not (The direction of transformation). Thus 1st law simply tells that if a process take place, energy will remain conserve. It doesn't tell us weather, the process is possible or not. The condition of transformation of heat into work (whether the process is possible or not) is specified by the 2nd law of thermodynamics. There are two equivalent statements of 2nd law of thermodynamics.

**Kelvin – Plank Statement :** It is impossible for a self acting device or machine unadded by any external agency to convert heat from a cold body to a hot body or heat can't flow spontaneously from a cold body to a hot body. Kelvin Plank and Clausis statement are equivalent. Any process which violates Kelvin Plank statement also violate Clausius statement. Any process which violate Kelvin-Plank and Clausius statement would also violate the principle of increase in entropy

$\therefore\ (\Delta S)_{\text{universe}} \geq 0$

$\rightarrow\ \Delta S = 0$ for Reversible process

$\Delta S > 0$ for irreversible or natural process.

$dS = \frac{dQ}{T}$ Mathematical form of 2nd law of thermodynamics

For reversible process $\Delta S = \oint \frac{dQ}{T} = 0$

The entropy of an isolated system can never decrease - entropy of a system measures the disorder of the system

## Carnot Theorem

**Ist Statement :** All the reversible engine working between source and sink have the same efficiency whatever the working substance

$$e_{R_1} = e_{R_2}$$

**2nd statement :** irreversible engine working between source and sink can never be more efficient then a reversible engine working between same source and sink

$$e_{R_1} = e_{R_2} > e_I$$

entropy of an isolated system can never decrease.

**Complete conversion of work into heat is possible but the reverse is not possible.**

**Heat engine:**

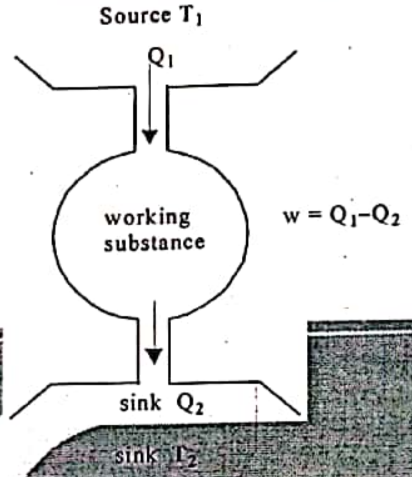
A cyclic device that converts heat taken from the source into mechanical work is called a heat engine.

**Parts of the engine :** (i) Source (ii) Sink (iii) working substance.
The net amount of work done by the substance $W = Q_1 - Q_2$

**Efficiency :** Efficiency of a heat engine is defined as the ratio of the work obtained to heat taken in form the source in one cycle.

$$\eta = \frac{W}{Q_1} = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1}$$

$\eta = 1$ when $Q_2 = 0$ i.e the sink is at absolute Zero which is impossible.



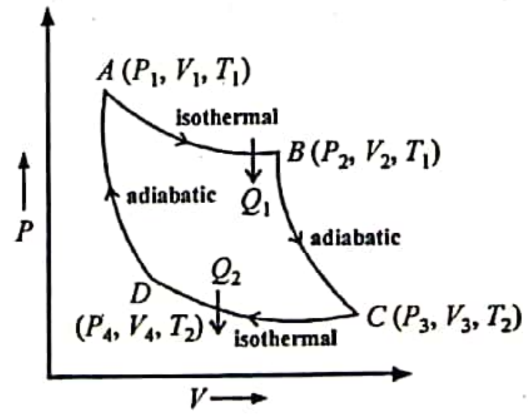
**Indicator diagram :**
The resultant PV diagram of a system undergoing a process is called indicator diagram. This diagram enables us to represent the working of an engine and to calculate useful work from the system (engine)

**Reversible engine :**
The engine based on reversible cycle is called reversible engine ( Carnot reversible engine).
(i) A cylinder with perfectly heat insulating walls but perfectly conducting base and closed with a tight fitting perfectly insulating and frictionless piston, filled with fixed mass of perfect gas as a working substance.
(ii) A hot body of infinitely large heat capacity at constant temperature $T_1$ (source)
(iii) A cold body of infinitely large heat capacity at constant temperature $T_2$ (sink)
(iv) A perfectly heat insulating stand.

$Q_1$ = heat taken from the source during Process AB
$Q_2$ = heat given to the sink from the system during process CD

Catnot's Cycle

$$\begin{cases} W_{AB} = Q_1 = \mu R T_1 \log\dfrac{V_2}{V_1} \\ W_{CD} = Q_2 = \mu R T_2 \log\dfrac{V_3}{V_4} \\ W_{BC} = \dfrac{\mu R}{\gamma - 1}(T_2 - T_1) \\ W_{DA} = \dfrac{\mu R}{\gamma - 1}(T_2 - T_1) \end{cases}$$



$$W = W_{AB} + W_{BC} + W_{CD} + W_{DA} = \mu R T_1 \log\frac{V_2}{V_1} + \mu R T_2 \log\frac{V_3}{V_4}$$

## Efficiency

$$\eta = \frac{W}{Q} = 1 - \frac{Q_2}{Q_1} \qquad \frac{Q_2}{Q_1} = \frac{T_2}{T_1} \log \frac{\frac{V_3}{V_4}}{\frac{V_2}{V_1}}$$

Since the curve BC and DA represents adiabatiac expansion and compression respectively.

$$TV^{\gamma-1} = \text{Const}$$

So $\quad T_1 V_2^{\gamma-1} = T_2 V_3^{\gamma-1}$ ... (i)

and $\quad T_1 V_1^{\gamma-1} = T_2 V_4^{\gamma-1}$ ... (ii)

Dividing $^{(i)}/_{(ii)}$, $\frac{V_2}{V_1} = \frac{V_3}{V_4} \Rightarrow \frac{Q_1}{Q_2} = \frac{T_1}{T_2}$

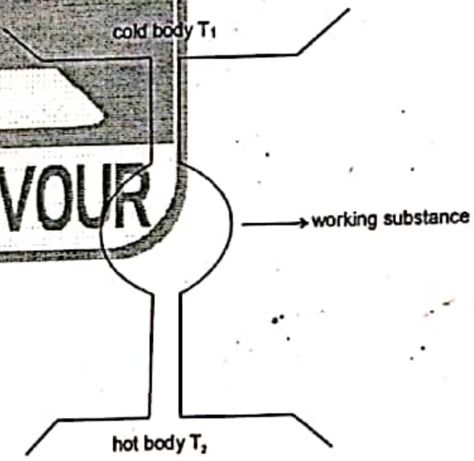
So $\quad \eta = 1 - \frac{Q_2}{Q_1}$ or $\eta = 1 - \frac{T_2}{T_1}$

## Refrigerator

A device that remove heat from a cold body and adding it to a hot body with the help of external agency. It is the reverse of heat engine.

**Co-efficient of performance of a refrigirator :**

It is the ratio heat taken in from the cold body to work done by external device need to run the refrigirator



$$K = \frac{Q_2}{W} = \frac{Q_2}{Q_1 - Q_2} = \frac{1}{\frac{Q_1}{Q_2} - 1}$$

But we know $\quad \frac{Q_1}{Q_2} = \frac{T_1}{T_2}$

So $\quad K = \frac{Q_2}{W} = \frac{Q_2}{Q_1 - Q_2} = \frac{T_2}{T_1 - T_2}$

Relation between efficiency of a carnot engine ($\eta$) and co-efficient of performance (K) :

$$\eta = \frac{T_1 - T_2}{T_1} \quad \text{and} \quad K = \frac{T_2}{T_1 - T_2}$$

Now $\quad K + 1 = \frac{T_1}{T_1 - T_2} \Rightarrow \frac{1}{K+1} = \frac{T_1 - T_2}{T_1} = \eta$

$$\boxed{\eta = \frac{1}{K+1}}$$

A good refrigerator should have a high co-efficient of performance.

## Entropy

One of the most common interpretation of entropy is done by saying that the entropy is the measure of disorderness of the system. It means more the orderness is present in the system less will be its entropy. Similarly, more the disorderness present in the system more will be its entropy. For example : The entropy of boiling water is more than the entropy of ice. Also, one of the common means for knowing the change in entropy of the system (for spontaneous-irreversible processes), is that the change in entropy will always be positive i.e., for irreversible spontaneous process the *entropy of the universe* always increases.

Mathematically the change in entropy for a reversible process is defined as

$$dS = \frac{đQ_R}{T}$$

$$\Rightarrow \int_{S_i}^{S_f} dS = \int_i^f \frac{đQ}{T} \quad \Rightarrow \boxed{\Delta S = S_f - S_i = \int_i^f \frac{đQ}{T}}$$

In the above definition $S$ is an exact differential. It means that just like internal energy the entropy is also state function. For the case of irreversible process, the change in entropy is calculated by replacing the irreversible process with a reversible process between the same initial and final states.

In order to understand the physical meaning of entropy and its significance, it is necessary to study *all* the entropy changes that take place when a system undergoes a reversible process. If we calculate the entropy change of the system and add the calculated entropy change of the surroundings, then we obtain the sum of the entropy changes brought about by this particular process. We may call this sum the *entropy change of the universe* due to the process in question.

The following table shows the calculation of change in entropy for various irreversible processes.

| Type of irreversibility | Irreversible process | Entropy change of the system | Entropy change of the local surroundings | Entropy change of the universe |
|---|---|---|---|---|
| External mechanical irreversibility | Isothermal dissipation of work through a system into internal energy of a reservoir | 0 | $\frac{W}{T}$ | $\frac{W}{T}$ |
| | Adiabatic dissipation of work into internal energy of a system | $C_P \ln\frac{T_f}{T_i}$ | 0 | $C_P \ln\frac{T_f}{T_i}$ |
| Internal mechanical irreversibility | Free expansion of an ideal gas | $nR \ln\frac{V_f}{V_i}$ | 0 | $nR \ln\frac{V_f}{V_i}$ |
| External thermal irreversibility | Transfer of heat through a medium from a hotter to a cooler reservoir | 0 | $\frac{Q}{T_2} - \frac{Q}{T_1}$ | $\frac{Q}{T_2} - \frac{Q}{T_1}$ |
| Chemical irreversibility | Diffusion of two dissimilar inert ideal gases | $2nR \ln\frac{V_f}{V_i}$ | 0 | $2nR \ln\frac{V_f}{V_i}$ |

**Isoentropic process :** A reversible process during which the entropy of a system remains constant is called isoentropy process.

According to 2nd law of thermodynamics $dQ = TdS$
For adiabatic process $dQ = 0 \Rightarrow dS = 0 \Rightarrow S = \text{constant}$
A reversible adiabatic process is an isoentropic process for irreversible process $dS > 0$.

**Q. From the law of thermodynamics prove the following relation $\left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$ and hence show that the internal energy of an ideal gas is independent of its volume but not so for an actual gas.**

**Soln.** I^st^ law of thermodynamics $dQ = dU + PdV$

2nd law of thermodynamics $dQ = T\,d\,S$

Combining these two laws $TdS = dU + PdV$

$$\Rightarrow \quad dS = \frac{1}{T}dU + \frac{P}{T}dV$$

Hence we can write at constant temperature

$$\left(\frac{\partial S}{\partial V}\right)_T = \frac{1}{T}\left(\frac{\partial U}{\partial V}\right)_T + \frac{P}{T} \Rightarrow T\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial U}{\partial V}\right)_T + P$$

Using Maxwell's thermodynamic relation $\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$ the above equation become

$$\therefore \quad T\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial U}{\partial V}\right)_T + P \quad \text{so} \quad \left(\frac{\partial U}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P \qquad \text{... (i)}$$

Now, from equation (i), we have

$$PV = RT \Rightarrow P = \frac{RT}{V} \Rightarrow \left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V}$$

Put this value in eqn (i)

$$\left(\frac{\partial U}{\partial V}\right)_T = T.\frac{R}{V} - P \Rightarrow \left(\frac{\partial U}{\partial V}\right)_T = P - P = 0 \quad \left(\because \frac{RT}{V} = P\right)$$

Hence internal energy of an ideal gas is independent of volume

(ii) $\left(P + \frac{a}{V^2}\right)(V - b) = RT \qquad P = \frac{RT}{V-b} - \frac{a}{V^2} \qquad \frac{\partial P}{\partial T} = \frac{R}{V-b}$

Put this value in eqn (i)

$$\left(\frac{\partial U}{\partial V}\right)_T = T.\frac{R}{V-b} - P = \frac{a}{V^2}$$

Hence internal energy of an real gas depends on volume. (All the above treatment is done for 1 mole of gas).

**Q. The mass M of a liquid at temperature $T_1$ is mixed with an equal mass of same liquid at temperature $T_2$. The system is thermally insulated. Show that the entropy change of the universe is $2MC_P \log_e \frac{T_1 + T_2}{2\sqrt{T_1T_2}}$.**

**Soln.** When M gm of the liquid at temperature $T_1$ is mixed with an equal mass of same liquid at temp $T_2$ the temperature of the mixture will be $\frac{T_1 + T_2}{2}$

Now change in entropy when the temp of one gm of liquid changes from $T_1$ to $\frac{T_1+T_2}{2}$

$$\Delta S_1 = \int_{T_1}^{\frac{T_1+T_2}{2}} \frac{dQ}{T} = \int_{T_1}^{\frac{T_1+T_2}{2}} MC_P \, dT/_T = MC_P \log_e \frac{T_1+T_2}{2T_1}$$

Also the change in entropy when the temp of M gm of liquid changes from $T_2$ to $\frac{T_1+T_2}{2}$

$$\Delta S_2 = \int_{T_2}^{\frac{T_1+T_2}{2}} MC_P \, dT/_T = MC_P \log_e \frac{T_1+T_2}{2T_2}$$

Hence the entropy change of the universe

$$\Delta S = \Delta S_1 + \Delta S_2$$

$$= MC_P \log_e \frac{T_1+T_2}{2T_1} + MC_P \log_e \frac{T_1+T_2}{2T_2}$$

$$= MC_P \log_e \left[\frac{T_1+T_2}{2T_1} \times \frac{T_1+T_2}{2T_2}\right]$$

$$= MC_P \log_e \left(\frac{T_1+T_2}{2\sqrt{T_1T_2}}\right)^2$$

$$\Delta S = 2MC_P \log_e \frac{T_1+T_2}{2\sqrt{T_1T_2}}$$

which is necessarily + Ve.

**Q.** **For an isobaric process prove the relation**

(i) $\left(\frac{\partial P}{\partial S}\right)_T \left(\frac{\partial S}{\partial T}\right)_P = -\left(\frac{\partial P}{\partial T}\right)_S$ (ii) $\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial P}{\partial T}\right)_V$

**Soln.** In the set of four thermodynamic variable (P, V, T, S) only two are independent variables while other two may be expressed as their functions.

We can represent pressure P as the function of two independent variables S and T i.e.

$$P = P(S,T) \Rightarrow dP = \left(\frac{\partial P}{\partial S}\right)_T dS + \left(\frac{\partial P}{\partial T}\right)_S dT$$

For an isobaric process dP = 0

Hence

$$\left(\frac{\partial P}{\partial S}\right)_T dS + \left(\frac{\partial P}{dT}\right)_S dT = 0$$

$$\left(\frac{\partial P}{\partial S}\right)_T dS = -\left(\frac{\partial P}{\partial T}\right)_S dT$$

$$\left(\frac{\partial P}{\partial S}\right)_T \left(\frac{\partial S}{\partial T}\right)_P = -\left(\frac{\partial P}{\partial T}\right)_S$$

(ii) Again we represent the pressure as the function of T and V

$$P = P(T, V)$$

$$dP = \left(\frac{\partial P}{\partial T}\right)_V dT + \left(\frac{\partial P}{\partial V}\right)_T dV$$

For an isobaric process dP = 0

$$\left(\frac{\partial P}{\partial T}\right)_V dT + \left(\frac{\partial P}{\partial V}\right)_T dV = 0$$

$$\left(\frac{\partial P}{\partial V}\right)_T dV = -\left(\frac{\partial P}{\partial T}\right)_V dT$$

$$\left(\frac{\partial P}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial P}{\partial T}\right)_V .$$

**Q. Prove the thermodynamic relation**

(i) $TdS = C_V dT + T\left(\frac{\partial P}{\partial T}\right)_V dV$ (ii) $TdS = C_P dT - T\left(\frac{\partial V}{\partial T}\right)_P dP$

**Soln.** (i) Let the entropy S of a thermodynamic system be a function of temperature T and volume V i.e.

$$S \equiv S(T, V)$$

Since dS is a perfect differential, we can write

$$dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$

Multiplying by T, we have

$$TdS = T\left(\frac{\partial S}{\partial T}\right)_V dT + T\left(\frac{\partial S}{\partial V}\right)_T dV \qquad \text{...(i)}$$

Since $TdS = dQ$

For any substance the specific heat at constant volume is given by

$$C_V = \left(\frac{\partial Q}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V .$$

From Maxwell's first relation

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

Making these substitution in eqn (i)

$$\boxed{TdS = C_V dT + T\left(\frac{\partial P}{\partial T}\right)_V dV} \Rightarrow \text{Required relation}$$

(ii) Let the entropy S of a thermodynamic system be function of temperature T and pressure P i.e

$$S = S(T, P)$$

Since dS is a perfect differential, we can write

$$dS = \left(\frac{\partial S}{\partial T}\right)_P dT + \left(\frac{\partial S}{\partial P}\right)_T dP$$

Multiplying by T

$$TdS = T\left(\frac{\partial S}{\partial T}\right)_P dT + T\left(\frac{\partial S}{\partial P}\right)_T dP \qquad \text{...(ii)}$$

For any substance the specific heat at constant pressure is

given by $C_P = \left(\frac{\partial Q}{\partial T}\right)_P = T\left(\frac{\partial S}{\partial T}\right)_P$

From Maxwell's II$^{nd}$ realtion $\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$

making these substitution in equation (ii)

$$\boxed{TdS = C_PdT - T\left(\frac{\partial V}{\partial T}\right)_P dP}$$

**Q.** **Find the efficiency of the Carnot engine working between the steam point and the ice point.**

**Soln.** Given $T_1 = 100°C = 100 + 273 = 373$ K $\qquad T_2 = 0°C = 0 + 273 = 273$ K

$$\eta = 1 - \frac{T_2}{T_1} = 1 - \frac{273}{373} = \frac{373 - 273}{373} = \frac{100}{373}$$

% of efficiency $= \frac{100}{373} \times 100 = 26.81\%$.

**Q.** **A carnot engine whose temperature of the source is 400 K takes 300 calories of heat at this temperature and reject 150 calories of heat to the sink. What is temperature of the sink. Also calculate the efficiency of the engine?**

**Soln.** $H_1 = 200$ Cal, $H_2 = 150$ Cal, $T_1 = 400$ K, $T_2 = ?$

$$\frac{H_1}{T_1} = \frac{H_2}{T_2} \Rightarrow T_2 = \frac{H_2}{H_1} \times T_1 = \frac{150}{200} \times 400 = 300K$$

$$\eta = 1 - \frac{T_2}{T_1} = 1 - \frac{300}{400} = 0.25$$

% of efficiency $0.25 \times 100 = 25\%$.

**Q.** **A carnot engine is operated between two reservoirs at temperature of 450 K and 350 K. If the engine receives 1000 calories of heat from the source in each cycle. Calculate the amount of heat rejected to the sink in each cycle. Calculate the efficiency of the engine & the work done by the engine in each cycle (1 calorie = 4.2J)**

**Soln.** $T_1 = 450°K$, $T_2 = 350°K$, $H_1 = 1000$ cal, $H_2 = ?$

$$\frac{H_2}{H_1} = \frac{T_2}{T_1} = H_2 = \frac{T_2}{T_1} \times H_1 = \frac{350}{450} \times 1000 = 777.77 \text{ cal.}$$

$$\eta = 1 - \frac{T_2}{T_1} = 1 - \frac{350}{450} = \frac{100}{450} = 0.2222$$

% of efficiency =22.22%

work done in each cycle $= H_1 - H_2$

$= 1000 - 777.77$ Cal $= 222.23 = 222.23 \times 4.2 = 933.335$ joule.

**Q.** **A carnot engine working as a refrigerator between 260 K and 300 K receives 500 calories of heat from the reservoir at the lower temperature calculate the amount of heat rejected to the reservoir at the higher temperature. Calculate also the amount of workdone in each cycle to operate the refrigerator.**

**Soln.** $Q_1 = ?$ $\qquad Q_2 = 500$ cal $\qquad T_1 = 260K \qquad T_2 = 300K$

$$\frac{Q_1}{T_1} = \frac{Q_2}{T_2} \quad \Rightarrow \quad Q_1 = \frac{Q_2}{T_2} \times T_1 = \frac{5000 \times 260}{300} = 576.92\text{cal}$$

$$W = Q_1 - Q_2 = 76.92 \text{ cal} = 76.42 \times 42 = 323.08 \text{ joule.}$$

**Q.** **A carnot's refrigerator takes heat from water at 0°C and discard it to a room at 27°C. 1 kg of water at 0°C is to be changed into ice at 0°C. How many calories of heat are discarded to the room? What is the work done by the refrigerator in this process? What is the co-efficient of performance of the machine?**

**Soln.** $Q_1 = ?$ $Q_2 = 1000 \times 80 = 80{,}000$ cal. $L = 80$ Cal/g (Latent heat of ice)

$T_1 = 300K$ $T_2 = 273°K$

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2} \Rightarrow Q_1 = \frac{T_1}{T_2} \times Q_2 = \frac{80000 \times 300}{273} = 87{,}900 \text{ cal.}$$

Work done by the refrigirator

$$W = J(Q_1 - Q_2) = 4.2(87900 - 80000)$$

$$= 4.2 \times 7900 = 3.183 \times 10^4 \text{ J}$$

$$\text{Co-efficient of performance} = \frac{Q_2}{Q_1 - Q_2} = \frac{80{,}000}{87900 - 80{,}000} = \frac{80{,}000}{7900} = 10.13$$

**Q.** **A carnot engine whose low temperature reservoir is at 7°C has an efficiency of 50%. It is desired to increase the efficiency to 70%. By how many degrees should the temperature of the high temperature reservoir be increased.**

**Soln.** $\eta = 50\% = 0.5,\ T_2 = 273 + 7 = 280\text{ K},\ T_1 = ?$

$$\eta = 1 - \frac{T_2}{T_1} = 0.5 = 1 - \frac{280}{T_1}$$

$$\frac{280}{T_1} = 0.5 \Rightarrow T_1 = \frac{280}{0.5} = \frac{2800}{5} = 560\text{ K}$$

In the 2nd case

$$\eta' = 70\% = 0.7$$

$$T_2 = 280K, \quad T_1 = ?$$

$$\eta' = 1 - \frac{T_2}{T_1}$$

$$0.7 = 1 - \frac{280}{T_1} \Rightarrow \frac{280}{T_1} = 0.3 \Rightarrow T_1 = \frac{280}{0.3} = 933.33\text{ K}$$

So increase in temperature = 933.33 − 560 = 372.33 K.

**Q.** **In a Carnot cycle, isothermal expansion of an ideal gas take place at 400 K and the isothermal compression at 300K. During the expansion 500 cal of heat energy are transfered to the gas. Determine**

**(1) The work performed by the gas during isothermal expansion.**

**(2) The heat rejected from the gas during an isothermal compression**

**(3) The work done in isothermal compression of gas**

**Soln.** (1) The work performed by the gas during the isothermal expansion is equivalent to heat $Q_1$ absorbed by the gas

Here, $Q_1 = W = 500$ cal

(2) Let $Q_2$ be the amount of heat rejected. Then,

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2} \Rightarrow Q_2 = \frac{T_2}{T_1} \times Q_1 = 500 \times \frac{300}{400} = 375\ cal$$

(3) The work done on the gas during isothermal compression is equivalent to the heat rejected

$$W = Q_2 = 375 \text{ cal}$$

**Q.** **Two identical bodies of constant heat capacities at temperature $T_1$ and $T_2$ $(T_1 > T_2)$ are used as reservoirs for a heat engine. Assuming that the bodies don't undergo any phase change and remain at constant pressure P. Show that the amount of work obtained is given by**

$$W = C_P(T_1 + T_2 - 2T_f)$$

**where $T_f$ is the final temperature of the bodies. Also show that W is maximum when $T_f = \sqrt{T_1T_2}$**

**Soln.** The working substance takes heat from the body at temperature $T_1$ and after doing work gives the balance heat to the body at temperature $T_2$. This process continues untill $T_1$ drops to $T_f$ and $T_2$ rises to $T_f$

The total heat taken from the hot body

$$Q_1 = C_P(T_1 - T_f) \quad \text{... (i)}$$

heat given to the cold body

$$Q_2 = C_P(T_f - T_2) \quad \text{... (ii)}$$

The balance $(Q_1 - Q_2)$ converts into work

$$W = Q_1 - Q_2 = C_P(T_1 - T_f) - C_P(T_f - T_2) \Rightarrow W = C_P(T_1 - T_f - T_f + T_2) = C_P(T_1 + T_2 - 2T_f)$$

The heat $Q_1$ is taken in at a mean temperature $= \frac{T_1 + T_f}{2}$

heat $Q_2$ is given out at a mean temperature $= \frac{T_2 + T_f}{2}$

Carnot engine have max efficiency so the work done must be maximum

$$\frac{Q_1}{Q_2} = \frac{\frac{T_1 + T_f}{2}}{\frac{T_2 + T_f}{2}} = \frac{T_1 + T_f}{T_2 + T_f}$$

From equation (i) and (ii)

$$\frac{Q_1}{Q_2} = \frac{T_1 - T_f}{T_f - T_2}$$

So $$\frac{T_1 + T_f}{T_2 + T_f} = \frac{T_1 - T_f}{T_f - T_2} \Rightarrow T_f = \sqrt{T_1T_2}$$

**Q.** **In a Carnot cycle, isothermal expansion of an ideal gas take place at 400 K and the isothermal compression at 300 K. During the expansion 500 cal of heat energy are transfered to the gas. Determine**

**(1) The work performed by the gas during isothermal expansion.**
**(2) The heat rejected from the gas during an isothermal compression**
**(3) The work done in isothermal compression of gas**

**Soln.** (1) The work performed by the gas during the isothermal expansion is equivalent to heat $Q_1$ absorbed by the gas

Here $Q_1 = 500 \text{ cal} = W$
$W = 500 \times 4.18 = 2090$ Joule.

(2) Let $Q_2$ be the amount of heat rejected

$$\frac{Q_1}{Q_2} = \frac{T_1}{T_2} \Rightarrow Q_2 = \frac{T_2}{T_1} \times Q_1 = 500 \times \frac{300}{400} = 375\text{K}$$

(3) The work done on the gas during isothermal compression is equivalent to the heat rejected

$$W = Q_2 = 375 \text{ cal} = 375 \times 4.18 = 1567.5 \text{ joule}$$

**Q.** **A reversible engine workes between two temperature whose difference is 100°C. If 746 J of heat from the source is taken and 546 J heat is given to the sink by working substance. Calculate the temperature of the source and sink?**

**Soln.** Given $T_1 - T_2 = 100 \qquad Q_1 = 746, \qquad Q_2 = 546$

use $\frac{Q_1}{Q_2}=\frac{T_1}{T_2} \Rightarrow \frac{Q_1}{Q_2}=\frac{746}{546}=\frac{373}{273}$

$$\frac{Q_1-Q_2}{Q_2}=\frac{T_1-T_2}{T_2} \Rightarrow \frac{200}{546}=\frac{100}{T_2} \Rightarrow T_2=\frac{546\times100}{200}=273$$

Now $T_1-T_2=100 \Rightarrow T_1=T_2+100=273+100=373.$

**Q. An ideal carnot heat engine takes 100 cal of heat at 627°C from a source and rejects a part at 27°C to the sink. Find the work done by the engine per cycle, the heat rejected to the sink per cycle & the efficiency of the engine.**

**Soln.** $Q_1=100$ cal $\quad T_1=627°C$
$Q_2=?$ $\quad T_2=27°C$

Let the temperature of the sink = x

Now $\frac{Q_1}{Q_2}=\frac{T_1}{T_2} \Rightarrow \frac{100}{x}=\frac{627}{27} \Rightarrow x=\frac{1000\times27}{627}=333.3$ cal

So the heat reject per cycle to the sink = 333.3 cal

Now $W=Q_1-Q_2=1000-333.3=666.7$ cal

Now, $\eta=1-\frac{T_2}{T_1}=1-\frac{27}{627}=\frac{600}{627}=\frac{200}{209}$

**Q. The efficiency of a carnot cycle is $\frac{1}{6}$, on reducing the temperature of the sink by 65°C the efficiency increases to $\frac{1}{3}$. Find the initial and final temperature between which the cycle it is working**

**Soln.** $1-\frac{T_2}{T_1}=\frac{1}{6} \Rightarrow \frac{T_1-T_2}{T_1}=\frac{1}{6} \Rightarrow 6T_1-6T_2=T_1$ or $5T_1-6T_2=0$ ...(i)

Now, $1-\frac{(T_2-65)}{T_1}=\frac{1}{3} \Rightarrow \frac{T_1-T_2+65}{T_1}=\frac{1}{3} \Rightarrow 3T_1-3T_2+195=T_1$

$\Rightarrow 2T_1-3T_2=-195$ ...(ii)

Solving eqn (i) and (ii)

$5T_1-6T_2=0$

$2T_1-3T_2=-195$

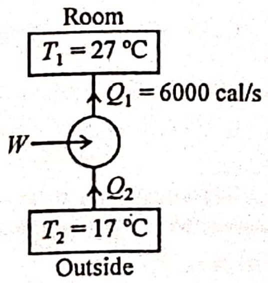
Solving, we have

$T_1=390$ K and $T_2=325$ K

**Q. On a winter day, when the temperature outside is 17°C the temperature inside a room is maintained at 27° C by using a heat pump. The heat pump compensates for the loss of heat due to the difference of temperature. If, for the temperatures given, the rate of heat loss is 6000 cal/s, what is the minimum rate of consumption of energy by the pump?**
**(a) 840 watt (b) 9300 watt (c) 15000 watt (d) 200 watt (e) 430 watt**

**Soln.** For minimum rate of consumption, the engine must be based on Carnot cycle and hence

$$\frac{Q_2}{Q_1}=\frac{T_2}{T_1}$$



$\therefore \quad Q_2=\frac{290}{300}\times6000=5800$ cal/s

$\therefore \quad W_{min}=Q_1-Q_2=200$ cal/s $=840$ W.

Correct option is (a)

**Q.** Two carnot engines are operating in series. The 1st engine absorbs a quantity of heat $Q_1$ at a temperature $T_1$ and after doing work $W_1$ rejects the remaining heat $Q_2$ at lower temperature $T_2$. The second engine absorbs the heat $Q_2$ at temperature $T_2$ (rejected by 1st) and after doing work $W_2$ rejects the remaining heat $Q_3$ at a still lower temperature $T_3$. Compute the efficiency of the combination.

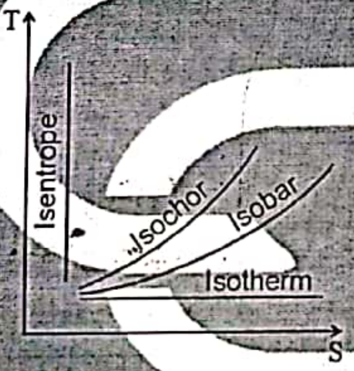
**Soln.** $W = (Q_1 - Q_2) + (Q_2 - Q_3) = Q_1 - Q_3$

$$\eta \text{ (efficiency)} = \frac{W}{Q_1} = \frac{Q_1 - Q_3}{Q_1} = 1 - \frac{Q_3}{Q_1}$$

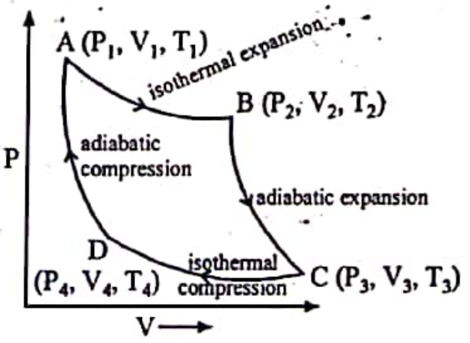
But, $\frac{Q_1}{Q_2} = \frac{T_1}{T_2}$ and $\frac{Q_1}{Q_3} = \frac{T_1}{T_3}$. So, $\eta = 1 - \frac{T_3}{T_1}$.

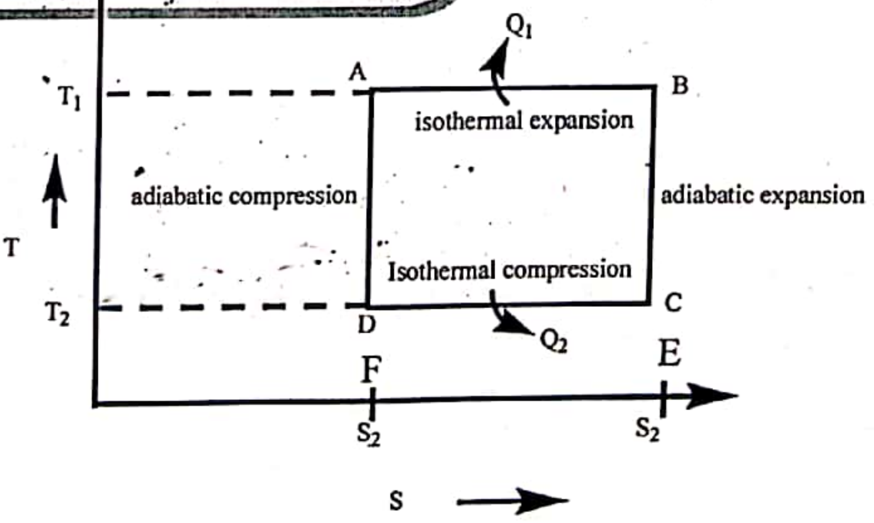
## T-S Diagram

Just like the PV-diagram is important for studying thermodynamics of an ideal gas, TS-diagram is important for studying the entropy changes taking place in various processes. The following figures schematically show the entropy changes taking place in various processes with the help of TS-curves.


T
Isentrope
Isochor
Isobar
Isotherm
S

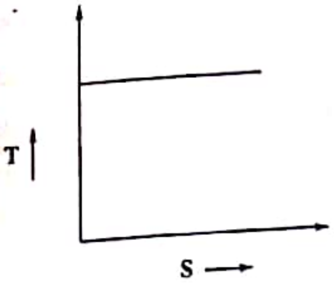
**T – S Curve for Carnot Engine :**


P
V
A (P1, V1, T1)
isothermal expansion
B (P2, V2, T2)
adiabatic compression
adiabatic expansion
D
(P4, V4, T4)
isothermal compression
C (P3, V3, T3)

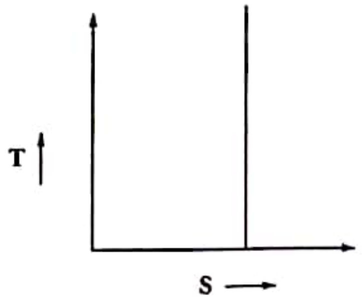

T
T1
T2
Q1
A
B
isothermal expansion
adiabatic compression
adiabatic expansion
Isothermal compression
C
D
Q2
F
E
S2
S2
S

**Area under PV curve represents amount of work done. Area of the cycle on T – S curve represent heat transfer.**

$$\eta = \frac{W}{Q} = \frac{\text{Area of ABCD}}{\text{Area of ABEF}}$$

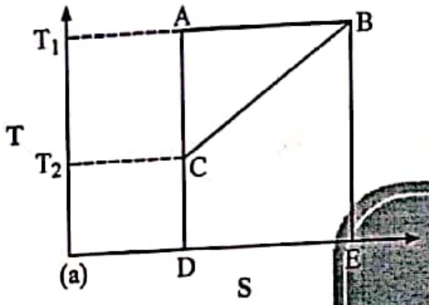


(Isothermal)

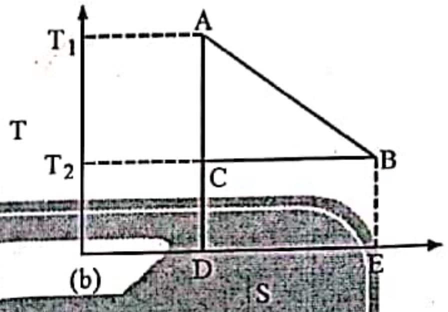


(Isentropic)

**Q.** **Compare the efficiency of the following cycles : →**



(a)



(b)

**Soln.** If $Q_1$ be the amount of heat absorbed during the process in which entropy increases and $Q_2$ be the amount of heat rejected during the process in which entropy decreases

$$\eta = \frac{Q_1 - Q_2}{Q_1} = \frac{\text{Area of ABC}}{\text{Area of ABED}}$$

Area of ABC for fig (a) = Area of ABC for fig (b)

Area of ABED for fig (A) > Area of ABED for fig (b)

$$\Rightarrow \eta_a < \eta_b$$

**Slope in T-S diagram:**

In a T–S diagram the slope of an isochoric process $= \frac{T}{C_V}$

In a T–S diagram the slope of an isobaric process $= \frac{T}{C_P}$

$$\frac{\text{Slope of isochoric}}{\text{Slope of isobaric}} = \frac{T/C_V}{T/C_P} = \frac{C_P}{C_V} = \gamma$$

**Q.** **Calculate the change in entropy when an ideal gas undergoes reversible isothermal expansion from initial volume $V_i$ to final volume $V_f$.**

**Soln.**
$$dQ = TdS \Rightarrow dS = \frac{dQ}{T}$$

$$\Delta S = S_f - S_i = \int_{V_i}^{V_f} \frac{dQ}{T}$$

According to first law of thermodynamics $dQ = dU + dW$

$dU = 0$ because the process is reversible–isothermal expansion

$$dQ = dW = PdV$$

So $\Delta S = \int_{Vi}^{V_f} \frac{PdV}{T}$

But we know $PV = \mu RT \Rightarrow \frac{P}{T} = \frac{\mu R}{V}$

$$\Delta S = \int_{Vi}^{V_f} \frac{\mu R}{V} dV = \mu R [\ell n\, V]_{V_i}^{V_f} = \mu R\ \ell n \frac{V_f}{V_i}$$

**Q. Calculate the change in entropy when a liquid is heated from $T_1$ to $T_2$ $(T_2 > T_1)$.**

**Soln.** Let a liquid of mass m specific heat C is heated from $T_1$ to $T_2$.

If dQ is the amount of heat taken by the liquid to rise its temperature by dT then

$$dQ = mCdT$$

Corresponding change in entropy

$$dS = \frac{dQ}{T} = \frac{mCdT}{T}$$

Entropy change in the entire process

$$(\Delta S)\ \text{liquid} = \int_{T_1}^{T_2} dS = \int_{T_1}^{T_2} mC \frac{dT}{T} = mC[\ell n\, T]_{T_1}^{T_2}$$

$$(\Delta S)\ \text{liquid} = mC\ \ell n \frac{T_2}{T_1}$$

Which is +ve($\because T_2 > T_1$). Thus entropy of liquid increases.

**Change in entropy on cooling :**

$$\Delta S = mC\ \ell n \frac{T_2}{T_1}$$

Here $T_2 < T_1$ (cooling). So the entropy of the liquid decreases

**Q. Calculate the change in entropy when ice (a) melts to water (b) changes into steam :**

**Soln.** (a) when ice changes to water at 0°C the change in entropy

$$\Delta S = \int \frac{dQ}{T} = \frac{Q}{T} = \frac{ML}{T}$$

where, M = mass of liquid, L = latent heat.

(i) The change in entropy when ice is converted in water at 0°C

$$\Delta S_1 = \frac{ML}{T_1},\quad \text{where } L = 80\ \text{kcal/gm}$$

The change in entropy when water is at 0°C and at 100°C

$$\Delta S_2 = mc\ \ell n \frac{T_2}{T_1}$$

The change in entropy when water at 100°C converted into steam

$$\Delta S_3 = \frac{mL}{T_2},\quad \text{where } L = 540\ \text{kcal/gm}$$

So total change in entropy

$$\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3 = \frac{mL}{T_1} + mc\ \ell n \frac{T_2}{T_1} + \frac{ml}{T_2}$$

**Q.** **A body of mass $m_1$, specific heat $c_1$ and temperature $T_1$ is thermally connected with another body of mass $m_2$, specific heat $c_2$ and at temperature $T_2$. Derive an expression for change in entropy.**

**Soln.** Let $T_1 > T_2$ and T be the equilibrium temperature

According to the principle of calorimetry

$$m_1c_1(T_1 - T) = m_2c_2(T - T_2)$$

$$m_1c_1T_1 - m_1c_1T = m_2c_2T - m_2c_2T_2$$

$$m_1c_1T + m_2c_2T = m_1c_1T_1 + m_2c_2T_2$$

$$T = \frac{m_1c_1T_1 + m_2T_2c_2}{m_1c_1 + m_2c_2}$$

The change in entropy when the body comes from $T_1$ to T

$$\Delta S_1 = m_1c_1 \int_{T_1}^{T} \frac{dT}{T} = m_1c_1 \ln \frac{T}{T_1} \qquad (T_1 > T)$$

The change in entropy when the body come from $T_2$ to T ($T_2 < T$)

$$\Delta S_2 = m_2c_2 \int_{T_2}^{T} \frac{dT}{T} = m_2c_2 \ln \frac{T}{T_2}$$

Total change in entropy $\Delta S = \Delta S_1 + \Delta S_2$

$$\Delta S = m_1c_1 \ \ln \frac{T}{T_1} + m_2c_2 \ln \frac{T}{T_2}$$

$$= \ln\left(\frac{T}{T_1}\right)^{m_1c_1} + \ln\left(\frac{T}{T_2}\right)^{m_2c_2}$$

$$\Delta S = \ln\left[\left(\frac{T}{T_1}\right)^{m_1c_1}\left(\frac{T}{T_2}\right)^{m_2c_2}\right] > 0$$

**Q.** **Derive an expression for the change in entropy of a perfect gas in terms of its pressure volume and specific heat undergoing on one mole of change in state.**

**Soln.** Let us consider one mole of perfect gas at pressure P, volume V and temperature T. When an infinitesimal amount of heat dQ is added to it the increase in entropy is

$$dS = \frac{dQ}{T}$$

From 1st law $dQ = dU + dW$

But $dU = C_V dT$ and $dW = PdV = RT\frac{dV}{V}$

so $$dQ = C_V dT + RT\frac{dV}{V}$$

$$dS = \frac{dQ}{T} = C_V \frac{dT}{T} + R\frac{dV}{V}$$

The total change in entropy

$$S = \int \frac{dQ}{T} = C_V \int \frac{dT}{T} + R\int \frac{dV}{V} \qquad \text{... (i)}$$

From ideal gas eqn. $PV = RT$

$$dT = \frac{PdV + VdP}{R}$$

and $R = C_p - C_V$

$$\therefore S = C_V \int \frac{PdV + VdP}{RT} + R\int \frac{dV}{V}$$

$$= C_V \int \frac{PdV + VdP}{PV} + (C_P - C_V)\int \frac{dV}{V}$$

$$= C_V \int \frac{dV}{V} + C_V\int \frac{dP}{P} + C_P \int \frac{dV}{V} - C_V \int \frac{dV}{V}$$

$$= C_V \int \frac{dP}{P} + C_P\int \frac{dV}{V}$$

$$\boxed{S = C_V \log P + C_P \log V + \text{constant}}$$

If a gas passes from an initial state $P_i, V_i, T_i$ to $P_f, V_f, T_f$ then the change in entropy of the gas is

$$\boxed{\Delta S = C_V \log \frac{P_f}{P_i} + C_P \log \frac{V_f}{V_i}}$$

**Q.** **Derive an expression for change in entropy of a perfect gas in terms of its temperature, pressure and specific heat at constant pressure.**

**Soln.** $dQ = dU + dW = C_V dT + PdV = C_V dT + RT\frac{dV}{V} = TdS$

$$dS = C_V \frac{dT}{T} + R\frac{dV}{V}$$

$$\Delta S = \int_i^f dS = \int_i^f \frac{C_V dT}{T} + R\int_i^f \frac{dV}{V} = C_V \ell n \frac{T_f}{T_i} + R\,\ell n \frac{V_f}{V_i}$$

Again $\frac{PV}{T} = \text{const} \Rightarrow \frac{P_i V_i}{T_i} = \frac{P_f V_f}{T_f} \Rightarrow \frac{V_f}{V_i} = \frac{P_i T_f}{P_f T_i}$

$$\Delta S = C_V\,\ell n \frac{T_f}{T_i} + R\,\ell n \frac{V_f}{V_i} = C_V\,\ell n \frac{T_f}{T_i} + R\,\ell n \frac{P_i}{P_f} + R\,\ell n \frac{T_f}{T_i}$$

$$= C_V\,\ell n \frac{T_f}{T_i} - R\,\ell n \frac{P_f}{P_i} + R\,\ell n \frac{T_f}{T_i}$$

$$= (C_P - R)\,\ell n \frac{T_f}{T_i} - R\,\ell n \frac{P_f}{P_i} + R\,\ell n \frac{T_f}{T_i}$$

$$= C_P\,\ell n \frac{T_f}{T_i} - R\,\ell n \frac{P_f}{P_i}$$

**Q.** **Calculate the change in entropy of a vander Waals' gas as its state changes from $(V_i, T_i)$ to $(V_f, T_f)$ where equation of state for one mole of vander Waals' gas is**

$\left(P + \frac{a}{V^2}\right)(V - b) = RT$ **where a, b are vander Waals' constants**

**Soln.** $dS = \frac{dQ}{T}$ : ($2^{nd}$ law of thermodynamics)

$dQ = dU + dW$ : ($1^{st}$ law of thermodynamics)

$$dU = C_V dT + \frac{a}{V^2}dV \text{ and } dW = PdV = \left(\frac{RT}{V-b} - \frac{a}{V^2}\right)dV$$

$$\text{So, } dS = \frac{dU + dW}{T} = \frac{C_V dT + \frac{RT}{(V-b)} dV}{T} = C_V \frac{dT}{T} + R\frac{dV}{V-b}$$

The change in entropy when the gas passes from the state $(V_i, T_i)$ to $(V_f, T_f)$ is:

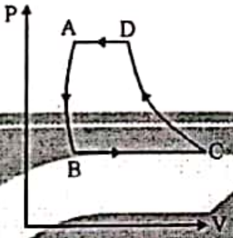
$$\Delta S = S_f - S_i = \int_i^f dS = C_V \int_i^f \frac{dT}{T} + R\int_i^f \frac{dV}{V-b}$$

$$= C_V \ln\frac{T_f}{T_i} + R\ln\frac{V_f - b}{V_i - b}$$

$$\boxed{\Delta S = C_V \ln\frac{T_f}{T_i} + R\ln\frac{V_f - b}{V_i - b}}$$

## PREVIOUS YEARS SOLUTIONS OF TIFR

**Q.** The pV diagram given below represents a **[TIFR 2010]**



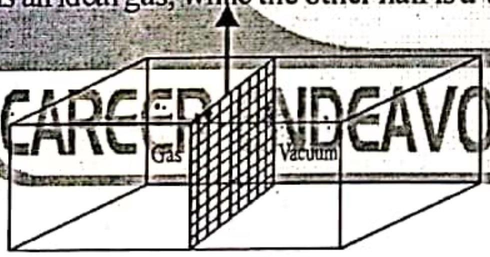
(a) Carnot refrigerator (b) Carnot engine

(c) gas turbine refrigerator (d) gas turbine engine

**Soln.** The gas turbine refrigerator and the gas turbine engine is governed by two isobaric and two adiabatic process. Now since the cycle is anti-clockwise, the pV-diagram in the question represents the gas turbine refrigerator.

**Correct option is (c)**

**Q.** Consider a sealed but thermally conducting container of total volume $V$, which is in equilibrium with a thermal bath at temperature $T$. The container is divided into two equal chambers by a thin but impermeable partition. One of these chambers contains an ideal gas, while the other half is a vacuum (see figure).



If the partition is removed and the ideal gas is allowed to expand and fill entire container, then the entropy per molecule of the system will increase by an amount **[TIFR 2012]**

(a) $2k_B$ (b) $k_B \ln(1/2)$ (c) $k_B \ln 2$ (d) $(k_B \ln 2)/2$

**Soln.** The first law of thermodynamic gives $dQ = dU + PdV$.

Since the container is in thermal equilibrium, $dU = 0$.

Therefore, $dQ = PdV$

$$\text{Therefore, } \Delta S = \int\frac{dQ}{T} = \int\frac{PdV}{T} = \int_{V/2}^{V} N k_B \frac{N}{V} = N k_B \ln 2.$$

So entropy change per molecule is $\Delta S = k_B \ln 2$.

**Correct option is (c)**

**Q.** A certain amount of fluid with heat capacity $C_F$ Joules/°C is initially at a temperature 0° C. It is then brought into contact with a heat bath at a temperature of 100° C, and the system is allowed to come into equilibrium. In this process, the entropy (in Joules / °C) of the Universe changes by **[TIFR 2013]**

(a) $100C_F$ (b) 0 (c) $0.055C_F$ (d) $0.044C_F$

**Soln.** The heat will flow from the heat bath to the fluid which is equal to $Q = C_F(373-273) = 100\,C_F$.

| Fluid $C_F$ | Heat bath |
|---|---|
| $T_F = 0\,^\circ\text{C}$ | $T_B = 100\,^\circ\text{C}$ |
| $= 273\text{ K}$ | $= 373\text{ K}$ |

Therefore, $(\Delta S)_{\text{fluid}} = \int \frac{dQ}{T} = C_F \int_{T_F}^{T_B} \frac{dT}{T} = C_F \ln\left(\frac{T_B}{T_F}\right) = C_F \ln\left(\frac{373}{273}\right)$

and $(\Delta S)_{\text{bath}} = \int \frac{dQ}{T} = \frac{1}{T_B}\int dQ = -\frac{Q}{T_B} = -\frac{100C_F}{373}$.

Therefore, $(\Delta S)_{\text{universe}} = (\Delta S)_{\text{fluid}} + (\Delta S)_{\text{bath}} = C_F \ln\left(\frac{373}{273}\right) - \frac{100}{373}C_F = 0.044\,C_F$.

**Correct option is (d)**

**Q.** The entropy $S$ of a black hole is known to be of the form **[TIFR 2013]**

$$S = \alpha k_B A$$

where $A$ is the surface area of the black hole and $\alpha$ is a constant, which can be written in terms of $c$ (velocity of light in vacuum), $\hbar$ (reduced Planck's constant) and $G_N$ (Newton's constant of gravitation).

Taking the radius of the black hole as $R = \frac{2G_N M}{c^2}$ it follows that the entropy $S$ is [$\lambda$ is a numerical constant]

(a) $\frac{G_N^2 M^2 k_B}{\lambda(\hbar c)^4}$ (b) $\frac{\hbar c k_B}{\lambda G_N M}$ (c) $\frac{G_N^2 M^2 k_B}{\lambda \hbar c^4}$ (d) $\frac{G_N M^2 k_B}{\lambda \hbar c}$

**Soln.** Given : $S = \alpha k_B A$, where $S$ has the same dimensions as $k_B$. So the dimension of $\alpha$ is $[M^{-2}]$.

Letting $\alpha = c^x \hbar^y G_N^z \Rightarrow \left[L^{-2}\right] = \left[LT^{-1}\right]^x \left[ML^2T^{-1}\right]^y \left[M^{-1}L^3T^{-2}\right]^z$

Solving, we get $x = 3$, $y = -1$ and $z = -1$.

Therefore, $\alpha = c^3 \hbar^{-1} G_N^{-1}$

Therefore, $S = \alpha k_B A = c^3 \hbar^{-1} G_N^{-1} k_B A$, where $A$ is the surface area of the blackhole.

So, $A = \beta R^2$, where $\beta$ is some numerical constant. $\Rightarrow S = \frac{c^3 k_B}{\hbar G_N}\beta\left(\frac{2G_N M}{c^2}\right)^2 = 4\beta\frac{G_N M^2 k_B}{\hbar c}$

Taking $4\beta = \frac{1}{\lambda}$, we have $S = \frac{G_N M^2 k_B}{\lambda \hbar c}$.

**Correct option is (d)**

## PREVIOUS YEARS SOLUTIONS OF JEST

**Q.** An ideal gas with adiabatic exponent $\gamma$ undergoes a process in which its pressure $P$ is related to its volume $V$ by the relation $P = P_0 - \alpha V$, where $P_0$ and $\alpha$ are positive constants. The volume starts from being very close to zero and increases monotonically to $P_0/\alpha$. At what value of the volume during the process does the gas have maximum entropy? [JEST 2016]

(a) $\frac{P_0}{\alpha(1+\gamma)}$ (b) $\frac{\gamma P_0}{\alpha(1-\gamma)}$ (c) $\frac{\gamma P_0}{\alpha(1+\gamma)}$ (d) $\frac{P_0}{\alpha(1-\gamma)}$

**Soln.** From first and second law of thermodynamics, we have

$$TdS = dU + PdV.$$

For maximum entropy, $dS = 0$.

$$\Rightarrow \quad dU + PdV = 0$$

$$\Rightarrow \quad \frac{f}{2}nR\,dT + PdV = 0$$

$$\Rightarrow \quad \frac{f}{2}(PdV + VdP) + PdV = 0$$

$$\Rightarrow \quad \left(\frac{f}{2}+1\right)PdV + \frac{f}{2}VdP = 0$$

where $P = P_0 - \alpha V$ or $dP = -\alpha dV$

Therefore, $\left(\frac{f}{2}+1\right)(P_0 - \alpha V)dV + \frac{f}{2}V(-\alpha dV) = 0$

$$\Rightarrow \quad \left(\frac{f}{2}+1\right)(P_0 - \alpha V) = \frac{f}{2}\alpha V \qquad [\because dV \neq 0]$$

$$\Rightarrow \quad V = \frac{\left(\frac{f}{2}+1\right)P_0}{\left(\frac{f}{2}+1\right)\alpha + \frac{f}{2}\alpha} = \frac{\left(\frac{f}{2}+1\right)P_0}{(f+1)\alpha}$$

where $\gamma = 1 + \frac{2}{f}$ or $f = \frac{2}{\gamma - 1}$

Therefore, $V = \frac{\left(\frac{1}{\gamma-1}+1\right)P_0}{\left(\frac{2}{\gamma-1}+1\right)\alpha} = \frac{\gamma}{\alpha(1+\gamma)}P_0$

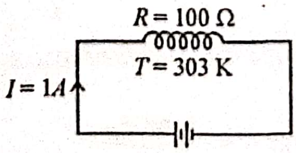
**Correct option is (c)**

**Q.** A 100 ohms resistor carrying current of 1 Amp is maintained at a constant temperature of 30°C by a heat bath. What is the rate of entropy increase of the resistor? [JEST 2014]

(a) 3.3 Joules/K/sec (b) 6.6 Joules/K/sec

(c) 0.33 Joules/K/sec (d) None of the above

**Soln.** The change in entropy is



$$\Delta S = \int \frac{dQ}{T} = \frac{1}{T}\int dQ = \frac{I^2 R \Delta t}{T}$$

$$\Rightarrow \quad \frac{\Delta S}{\Delta t} = \frac{I^2 R}{T} = \frac{(1)^2(100)}{303} = 0.33\ \text{JK}^{-1}\ \text{sec}^{-1}.$$

**Correct option is (c)**

**Q.** Consider a ideal gas of mass 'm' at temperature $T_1$ which is mixed isobarically (i.e. at constant pressure) with an equal mass of same gas at temperature $T_2$ in a thermally insusulated container. What is the change of entropy of the universe? **[JEST 2012]**

(a) $2mC_p \ln\left(\frac{T_1+T_2}{2\sqrt{T_1T_2}}\right)$ (b) $2mC_p \ln\left(\frac{T_1-T_2}{2\sqrt{T_1T_2}}\right)$ (c) $2mC_p \ln\left(\frac{T_1+T_2}{2T_1T_2}\right)$ (d) $2mC_p \ln\left(\frac{T_1-T_2}{2\sqrt{T_1T_2}}\right)$

**Soln.**

| | |
|---|---|
| $m, T_1, C_p$ | $m, T_2, C_p$ |

If $C_p$ be the specific heat of the both gases and $T_f$ be the final temperature, the principle of calorimetry gives $m_1 C_{p_1}(T_f - T_1) = -m_2 C_{p_2}(T_f - T_2)$, where $m_1 = m_2 = m$ and $C_{p_1} = C_{p_2} = C_p$.

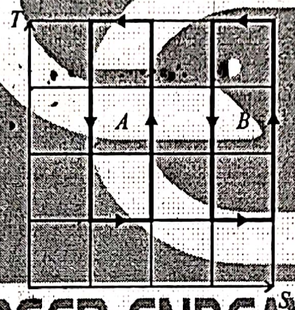
Therefore, $T_f = \frac{T_1+T_2}{2}$. The change in the entropy of the universe is

$$\Delta S = \Delta S_1 + \Delta S_2 = \int_{T_1}^{T_f} \frac{dQ}{T} + \int_{T_2}^{T_f} \frac{dQ}{T} = mC_p \ln\frac{T_f}{T_1} + mC_p \ln\frac{T_f}{T_2}$$

$$= mC_p \ln\left(\frac{T_f^2}{T_1T_2}\right) = mC_p \ln\left[\frac{(T_1+T_2)^2}{4T_1T_2}\right] = 2mC_p \ln\left(\frac{T_1+T_2}{2\sqrt{T_1T_2}}\right).$$

**Correct option is (a)**

**Q.** The entropy temperature diagram of two Carnot engines, $A$ and $B$, are shown in the figure 5. The efficiencies of the engines are $\eta_A$ and $\eta_B$ respectively. Which one of the following equalities is correct ? **[JEST 2015]**



(a) $\eta_A = \eta_B/2$ (b) $\eta_A = \eta_B$ (c) $\eta_A = 3\eta_B$ (d) $\eta_A = 2\eta_B$

**Soln.** The efficiency of a Carnot engine depends only on the temperature of the source $(T_1)$ and of the sink $(T_2)$ as

$$\eta = 1 - \frac{T_2}{T_1}$$

Since the values of $T_1$ and $T_2$ are same for both engines $A$ and $B$, $\eta_A = \eta_B$.

**Correct option is (b)**

# Chapter 4

# Maxwell's relations & thermodynamic potentials

## Maxwell's Thermodynamics Relations

From 1st law of thermodynamics

$$dQ = dU + dW \qquad \text{... (i)}$$

where dQ is the amount of heat absorbed in reversible process

The change in entropy is given by

$$dS = \frac{dQ}{T} \qquad \text{... (ii)}$$

From eqn (i) & (ii)

$$dU = TdS - PdV$$

So $$\frac{\partial^2 u}{\partial y\,\partial x} = \frac{\partial}{\partial y}\left(T\frac{\partial S}{\partial x} - P\frac{\partial V}{\partial x}\right)$$

$$= T\frac{\partial^2 s}{\partial y\partial x} + \frac{\partial T}{\partial y}\frac{\partial S}{\partial x} - P\frac{\partial^2 v}{\partial y dx} - \frac{\partial P}{\partial y}\frac{\partial V}{\partial x} = T\frac{\partial^2 S}{\partial y\partial x} - P\frac{\partial^2 V}{\partial y\partial x} + \frac{\partial T}{\partial y}\frac{\partial S}{\partial x} - \frac{\partial P}{\partial y}\frac{\partial V}{\partial x}$$

Thus, $$\frac{\partial^2 U}{\partial x\partial y} = T\frac{\partial^2 S}{\partial x\partial y} - P\frac{\partial^2 V}{\partial x\partial y} + \frac{\partial T}{\partial x}\frac{\partial S}{\partial y} - \frac{\partial P}{\partial x}\frac{\partial V}{\partial y}$$

But $$\frac{\partial^2 U}{\partial y\partial x} = \frac{\partial^2 U}{\partial x\partial y} \text{ and } \frac{\partial^2 S}{\partial x\partial y} = \frac{\partial^2 S}{\partial y\partial x} \text{ and } \frac{\partial^2 V}{\partial x\partial y} = \frac{\partial^2 V}{\partial y\partial x}$$

Hence $$\left(\frac{\partial T}{\partial y}\right)_x\left(\frac{\partial S}{\partial x}\right)_y - \left(\frac{\partial P}{\partial y}\right)_x\left(\frac{\partial V}{\partial x}\right)_y = \left(\frac{\partial T}{\partial x}\right)_y\left(\frac{\partial S}{\partial y}\right)_x - \left(\frac{\partial P}{\partial x}\right)_y\left(\frac{\partial V}{\partial y}\right)_x \qquad \text{... (iii)}$$

**1st relation :** $x = T$ $\quad y = V$

$$\frac{\partial T}{\partial x} = 1 \qquad \frac{\partial V}{\partial y} = 1 \qquad \frac{\partial T}{\partial y} = 0 \qquad \frac{\partial V}{\partial y} = 0$$

**Substituting in eqn. (iii)** $$\boxed{\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V}$$

**2nd relation :** $x = T$ $\quad y = P$

$$\frac{\partial T}{\partial x} = \frac{\partial P}{\partial y} = 1 \qquad \frac{\partial T}{\partial y} = \frac{\partial P}{\partial x} = 0$$

**Substituting in eqn. (iii)** $$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

$$dS = \frac{1}{T}dQ \quad \Rightarrow \quad \boxed{\left(\frac{dQ}{\partial P}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_P}$$

**3rd relation :** $x = S$ $\quad y = V$

$$\frac{\partial S}{\partial x} = \frac{\partial V}{\partial y} = 1 \qquad \frac{\partial S}{\partial y} = \frac{\partial V}{\partial x} = 0$$

**Substituting in eqn (iii)** $\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$

or $\boxed{\left(\frac{\partial T}{\partial V}\right)_S = -T\left(\frac{\partial P}{\partial Q}\right)_V}$

**4th relation :** $x = S$ $\quad y = P$

$$\frac{\partial S}{\partial x} = \frac{\partial P}{\partial y} = 1 \quad \text{and} \quad \frac{\partial S}{\partial y} = \frac{\partial P}{\partial x} = 0$$

**Substituting in eqn. (iii)**

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P \quad \text{or} \quad = \boxed{\left(\frac{\partial T}{\partial P}\right)_S = T\left(\frac{\partial V}{\partial Q}\right)_P}$$

**5th relation :** $x = P$ $\quad y = V$ $\quad \frac{\partial P}{\partial x} = \frac{\partial V}{\partial S} = 1 \quad \frac{\partial P}{\partial y} = \frac{\partial V}{\partial x} = 0$

**Substituting in eqn (iii)** $\left(\frac{\partial T}{\partial P}\right)\left(\frac{\partial S}{\partial V}\right) - \left(\frac{\partial T}{\partial V}\right)\left(\frac{\partial S}{\partial P}\right) = 1$

**6th relation :** $x = T$ $\quad y = S$ $\quad \frac{\partial T}{\partial x} = \frac{\partial S}{\partial y} = 1 \quad \frac{\partial T}{\partial y} = \frac{\partial S}{\partial x} = 0$

**Substituting in eqn. (iii)**

$$\left(\frac{\partial P}{\partial T}\right)_S\left(\frac{\partial V}{\partial S}\right)_T - \left(\frac{\partial P}{\partial S}\right)_T\left(\frac{\partial V}{\partial T}\right)_S = 1$$

## Helmholtz function or Helmholtz free energy (F)

It is also called as thermodynamical potential at constant volume. It is defined by the equation

$$F = U - TS$$

Since U, T and S are perfect differentials, F is also a perfect differential. When a system undergoes an infinitesinal reversible change from an initial equilibrium state to a final equilibrium state, the Helmholtz energy changes by an amount given by

$$dF = dU - TdS - SdT \qquad \text{But } dU = TdS - PdV$$

$$= TdS - PdV - TdS - SdT = -PdV - SdT$$

Taking the partial differentiation of F, we have

$$\left(\frac{\partial F}{\partial T}\right)_V = -S \qquad \left(\frac{\partial F}{\partial V}\right)_T = -P$$

Since dF is a perfect differential, we have

$$\left[\frac{\partial}{\partial V}\left(\frac{\partial F}{\partial T}\right)_V\right]_T = \left[\frac{\partial}{\partial T}\left(\frac{\partial F}{\partial V}\right)_T\right]_V \Rightarrow \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V \rightarrow \text{Maxwell's I}^{st} \text{ relation}$$

## Enthalpy or total heat function (H)

It is defined by $H = U + PV$

When a system undergoes an infinitesimal reversible change from an initial equilibrium state to a final equilibrium state, the enthalpy changes by an amount given by

$dH = dU + PdV + VdP$ But $dU = TdS - PdV$

$dH = TdS - PdV + PdV + VdP = TdS + VdP$

Taking the partial differentiation of H we have

$$\left(\frac{\partial H}{\partial S}\right)_P = T \text{ and } \left(\frac{\partial H}{\partial P}\right)_S = V$$

Since dH is a perfect differential, we have $\left[\frac{\partial}{\partial P}\left(\frac{\partial H}{\partial S}\right)_P\right]_S = \left[\frac{\partial}{\partial S}\left(\frac{\partial H}{\partial P}\right)_S\right]_P$

Or $\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$ → Maxwell's Fourth relation

## Gibbs function or Gibbs free energy (G)

It is also called as thermodynamic potential at constant pressure. It is defined by

$G = H - TS = U + PV - TS$

For an infinitesimal reversible process, we have

$dG = dU + PdV + VdP - TdS - SdT$

$= TdS - PdV + PdV + VdP - TdS - SdT$

$= VdP - SdT$

The partial differentiation of G gives

$$\left(\frac{\partial G}{\partial P}\right)_T = V \text{ and } \left(\frac{\partial G}{\partial T}\right)_P = -S$$

Since dG is a perfect differential so we have $\left[\frac{\partial}{\partial T}\left(\frac{\partial G}{\partial P}\right)_T\right]_P = \left[\frac{\partial}{\partial P}\left(\frac{\partial G}{\partial T}\right)_P\right]_T$ $\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T$

**Importance :**

(1) Thermodynamic functions are of practical importance in studying the condition of equilibrium of a system e.g., the condition of equilibrium for a process in which the temperature and volume of the system remain constant (Isothermal-Isochoric) may be expressed as

$dF = 0$ $(\because dF = -PdV - SdT)$.

This means that out of various states which a system can assume by isothermal isochoric process, only those are stable in which the Helmholtz free energy ( $F = U - TS$ ) is a minimum

The equation $dF = 0$ refers to a minimum value of F (and not to a maximum value). It follows from the fact that in any natural (irreversible) process the Helmholtz free energy can only fall because the entropy can only increase.

Similarly the condition of equilibrium for a process in which the temperature and pressure of the system remain constant (isothermal isobaric process) may be expressed as

$dG = 0$ $(\because dG = VdP - SdT)$

This means that a system at constant temperature and pressure is in stable equilibrium when the Gibbs function G (the thermodynamic potential of constant pressure) is a minimum.

**Physical significance of Helmholtz free energy : (A Helmholtz free energy)**

(1) $A = U - TS \Rightarrow TS = U - A \rightarrow$ Latent energy or bound energy of the system. As it can't be used in useful form (work)

(2) For isothermal reversible process

$-dA = PdV = dW$

The Helmholtz free energy is the energy decrease in which (–dA) gives the maximum amount of work (dW) done by the system during an isothermal change from initial state to final state. It is also called thermodynamic potential at constant volume.

$$A = U - TS \Rightarrow A = U + T\left(\frac{\partial A}{\partial T}\right)_V \rightarrow \text{Gibbs-Helmholtz relation}$$

## Physical Significane of Enthalpy

(1) $dH = TdS$ ( at constant P)

Enthalpy represents the quantity of heat given to the system at constant pressure. So it is called heat contained or total heat function

## Physical Significance of Gibbs Function

$$dG = VdP - SdT$$
$$= -dW - SdT + PdV + VdP$$

$-dG = dW - PdV$ ( For isothermal isobaric process)

Gibbs free energy is such that decrease in it gives the maximum non-PdV work which can be obtained from the system other than that due to change in volume for isothermal isobaric process. This is also known as thermodynamic potential at constant pressure

$G = H - TS$

$$G = H + T\left(\frac{\partial G}{\partial T}\right)_P \rightarrow \text{Gibbs-Helmholtz relation}$$

**Two important derivations.**

(i) $\left(\frac{\partial C_V}{\partial V}\right)_T = T\left(\frac{\partial^2 P}{\partial T^2}\right)_V$ (ii) $\left(\frac{\partial C_P}{\partial P}\right)_T = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_P$

(i) We Know Maxwell's Relations not given in prior from Maxwell's equation.

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

Diffrentiating w.r.t. T at constant volume

$$\left[\frac{\partial}{\partial T}\left(\frac{\partial S}{\partial V}\right)_T\right]_V = \left(\frac{\partial^2 P}{\partial T^2}\right)_V$$

Since for a state function, second order differentials are independent of order of differentiation :

$$T\left[\frac{\partial}{\partial V}\left(\frac{\partial S}{\partial T}\right)_V\right]_T = T\left(\frac{\partial^2 P}{\partial T^2}\right)_V \qquad \text{(multiplying with T on both sides)}$$

$$\left[\frac{\partial}{\partial V}\left(\frac{\partial Q}{\partial T}\right)_V\right]_T = T\left(\frac{\partial^2 P}{\partial T^2}\right)_V \qquad (\because dQ = TdS)$$

$$\left(\frac{\partial C_V}{\partial V}\right)_T = T\left(\frac{\partial^2 P}{\partial T^2}\right)_V$$ (using definition of $C_V$)

(ii) From Maxwell's equation.

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

Diffrentiating w.r.t. T at constant pressure

$$\left[\frac{\partial}{\partial T}\left(\frac{\partial S}{\partial P}\right)_T\right]_P = -\left(\frac{\partial^2 V}{\partial T^2}\right)_P$$

Multiplying both sides by T

$$T\left[\frac{\partial}{\partial P}\left(\frac{\partial S}{\partial T}\right)_P\right]_T = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_P$$

$$\left[\frac{\partial}{\partial P}\left(\frac{\partial Q}{\partial T}\right)_P\right]_T = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_P$$

$$\left(\frac{\partial C_P}{\partial P}\right)_T = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_P$$ (using definition of $C_P$).

**Q. Establish the following thermodynamic relation**

$$\left(\frac{\partial Q}{\partial P}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_P = -TV\alpha$$

**where $\alpha$ in the coefficient of volume expansion at constant pressure. Hence show that increase in pressure heats a body that expands with rise of temperature and colds that contracts on heating.**

**Soln.** The Maxwell thermodynamic relation is:

$$\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P$$

Multiplying by T both side

$$T\left(\frac{\partial S}{\partial P}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_P \Rightarrow \left(\frac{\partial Q}{\partial P}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_P \quad (dQ = TdS)$$

$$\Rightarrow \left(\frac{\partial Q}{\partial P}\right)_T = -TV\frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \Rightarrow \left(\frac{\partial Q}{\partial P}\right)_T = -TV\alpha$$

where $\alpha = 1/V\left(\frac{\partial V}{\partial T}\right)_P$ is the coefficient of volume expansion

(i) If substance expands with rise in temperature then, $\alpha$ will be positive

Hence $\left(\frac{\partial Q}{\partial P}\right)_T = -\text{Ve}$

If we increase the pressure, $\partial Q$ at constant temperature will be negative. So, to maintain temperature constant heat must be drawn from the system. It means increase in pressure will heat the system.

(ii) If substance contracts with rise in temperature then $\alpha$ will be negative

$$\left(\frac{\partial Q}{\partial P}\right)_P = +\text{Ve}$$

If we increase the pressure $(\partial Q)_T$ will be positive. So, to maintain temperature constant heat must be given to the system. It means increase in pressure will cool the system.

**Q.** **Prove the Clausius-Clapeynon equation** $\frac{dP}{dT} = \frac{mL}{T(V_2 - V_1)}$

**Soln.** The Maxwell's relation gives

$$\therefore \quad \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

Multiplying both sides by T we get

$$T\left(\frac{\partial S}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V \qquad \text{where } TdS = dQ$$

$$\therefore \quad \left(\frac{\partial Q}{\partial V}\right)_T = T\left(\partial P/\partial T\right)_V \qquad \text{... (i)}$$

Here dQ is the heat absorbed at constant temperature

$\therefore$ dQ is the latent heat

Thus if a body of mass 'm' and latent heat 'L' absorbs an amount of heat to change its state at constant temperature T and volumes in the I^st^ and the 2^nd^ states are $V_1$ and $V_2$

Eqution (i) reduces to

$$\frac{mL}{V_2 - V_1} = T\frac{dP}{dT}$$

or $$\boxed{\frac{dP}{dT} = \frac{mL}{T(V_2 - V_1)}} \rightarrow \text{Clausius-Clapeyron eqn.}$$

**Q.** The internal energy U is related to the Helmholtz free energy F by the relation:

(a) $U = -T\left\{\frac{\partial^2}{\partial T^2}\left(\frac{F}{T}\right)\right\}_V$ (b) $U = T\left\{\frac{\partial^2}{\partial T^2}\left(\frac{F}{T}\right)\right\}_V$

(c) $U = -T^2\left\{\frac{\partial}{\partial T}\left(\frac{F}{T}\right)\right\}_V$ (d) $U = T^2\left\{\frac{\partial}{\partial T}\left(\frac{F}{T}\right)\right\}_V$

**Soln.** We have

$$\left[\frac{\partial}{\partial T}\left(\frac{F}{T}\right)\right]_V = \left[\frac{\partial}{\partial T}\left(\frac{U - TS}{T}\right)\right]_V$$

$$= \frac{1}{T}\left(\frac{\partial U}{\partial T}\right) - \frac{U}{T^2} - \left(\frac{\partial S}{\partial T}\right)_V$$

where $T\left(\frac{\partial S}{\partial T}\right)_V = \left(\frac{\partial Q}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V$

Therefore, $U = -T^2\left[\frac{\partial}{\partial T}\left(\frac{F}{T}\right)\right]_V$

**Correct option is (c)**

**Q.** **A certain system found to have a Gibb's free energy is given by $G(P,T) = RT\ell n\left[\frac{aP}{(RT)^{5/2}}\right]$, where $a$ and R are constants. Find the entropy and specific heat at constant pressure.**

**Soln.** $G(P,T) = RT\ell n\left[\frac{aP}{(RT)^{5/2}}\right]$

$$S = -\left(\frac{\partial G}{\partial T}\right)_P = \frac{5}{2}R - R\,\ell n\left[\frac{aP}{(RT)^{5/2}}\right]$$

So, $C_P = \left(\frac{\partial Q}{\partial T}\right)_P = T\left(\frac{\partial S}{\partial T}\right)_P = \frac{5R}{2}$

## PREVIOUS YEARS SOLUTIONS OF TIFR

**Q.** The equation of state of a gas is given by $V = \frac{RT}{P} - \frac{b}{T}$, where $R$ is the gas constant and $b$ is another constant parameter. The specific heat at constant pressure $C_P$ and the specific heat at constant volume $C_V$ for this gas is related by $C_P - C_V =$ **[TIFR 2015]**

(a) $R$ (b) $R\left(1+\frac{RT^2}{bP}\right)^2$ (c) $R\left(1+\frac{bP}{RT^2}\right)^2$ (d) $R\left(1-\frac{bP}{RT^2}\right)^2$

**Soln.** The given equation is $V = \frac{RT}{P} - \frac{b}{T}$ ...(1)

Equation (1) gives,

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P} + \frac{b}{T^2} = \frac{RT^2 + bP}{PT^2} \quad \text{...(2)}$$

Equation (1) can also be written as

$$\frac{RT}{P} = V + \frac{b}{T} = \frac{VT+b}{T} \text{ or } P = \frac{RT^2}{VT+b} \quad \text{...(3)}$$

Therefore, $\left(\frac{\partial P}{\partial T}\right)_V = \frac{(VT+b)(2RT) - (RT^2)(V)}{(VT+b)^2}$

$$= \frac{RT^2V + 2RbT}{(VT+b)^2} \quad \text{...(4)}$$

The general relation of $C_p - C_v$ is given by

$$C_p - C_v = T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P = T\left(\frac{RT(TV+2b)}{(TV+b)^2}\right)\left(\frac{RT+bP}{PT}\right)$$

From (3), we get

$$TV = \frac{RT^2 - Pb}{P}.$$

Therefore, $$C_p - C_v = T\left[\frac{RT\left(\frac{RT^2 - Pb}{P} + 2b\right)}{\left(\frac{RT^2 - Pb}{P} + b\right)^2}\right]\left(\frac{RT^2 + Pb}{PT^2}\right)$$

$$= \left(\frac{RT + Pb}{PT}\right)\left(\frac{RT\left(\frac{RT^2 + Pb}{P}\right)}{\left(\frac{RT^2}{P}\right)^2}\right)$$

$$= \left(\frac{RT^2 + Pb}{RT^4}\right)\left(RT^2 + Pb\right)^2$$

$$= \frac{1}{RT^4}\left(RT^2 + Pb\right)^2$$

$$= R\left(1 + \frac{Pb}{RT^2}\right)^2$$

Correct option is (c)